NANYANG
TECHNOLOGICAL
UNIVERSITY

**PROGRAMMABLE NANOMATERIALS FOR HEALTH-
RELATED FLEXIBLE SENSING ELECTRONICS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

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

2017

Statement of Originality

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

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Date

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Abstract

Health-related flexible sensing electronics and wearable/attachable personal health monitoring systems will change the conventional diagnose method in clinical practice, and promote the revolution of next medical instruments towards portable, wearable, remote, and timely. As a crucial component, smart flexible sensing electronics can real-timely tracking physiological signals which are tightly associated with body conditions, such as heart rate, wrist pulse, body temperature, blood/intraocular pressure, and blood/sweat bio-information. Monitoring such physiological signals provide a convenient and non-invasive way for disease diagnoses and health assessments. However, the use of conventional materials and technology is yet rather limited because of their poor portability, biocompatibility, as well as high power consumptions.

To bring flexible electronic device towards smaller, smart, and less power consumption, as well as multi-functionality, this PhD thesis focuses on developing the novel programmable nanomaterials and new device configurations for next health-related flexible sensing electronics. Three new nanomaterials, including programmable carbon patterns, self-crosslinked carbon arrays, and ultra-thin CdS films, were developed for flexible sensing electronics. Some fundamental issues, such as growth mechanism of materials, the interface synergistic effects between each functional material for entire flexible sensing device, and the electromechanical interaction were investigated.

In the first study, inspiring from the conventional photolithography process, a novel and effective method have been developed for the synthesis of high-quality micro-patterned carbon by pre-patterning pyrolyzed photoresist as the solid carbon precursors. This method can produce high crystallinity carbon patterns with a high lateral resolution of $\sim 2\text{ }\mu\text{m}$, which approaches to the limit resolution of the traditional near-UV photolithography (at hard contact mode) and meets the requirement of the most flexible electronics. Also, bendable electronic devices have been fabricated based on the high-quality micro-patterned carbon. The bendable carbon device can suffer the bending angle from 0° to 180° and

presents distinct output response for tensile and compressive strain and high sensitivity, which makes it promise in the construction of flexible mechanical sensors.

In the following works, a novel carbon nanorod array (CA) that is characterized as vertically aligned nanorods and self-crosslinked junctions was reported. Comparing with 2-dimensional (2D) networks and solid thin films, such geometries are highly resistant to crack and fragmentation under stain. In the meantime, it shows high sensitivity and good stability ($\sim 10,000$ times) to detect the flexions. This CA-based flexible devices can record low frequency vibrations (< 6 Hz) and make it excellent to monitor the rest tremor of human body, which is an initial symptom of Parkinson's disease. Therefore, this self-crosslinked CA can be used to fabricate cost-effective and durable flexible sensor for early diagnosis of disease by monitoring the health-related rest tremors.

Piezoelectric materials are promising in applications of accurate pressure/strain sensors. In the third study, the CdS thin films with the thickness of 2~3 nm were synthesized using chemical vapor deposition method, and demonstrated the vertical piezoelectricity d_{33} of CdS in atomic scale (3~5 space lattices) by single and dual-frequency resonance tracking piezoelectric force microscopy (DART-PFM). The surface potential and charge distribution was measured by SKFM. The vertical piezoelectric domains at the CdS thin films was observed, and the measured piezoelectric coefficient (d_{33}) of $32.8 \text{ pm} \cdot \text{V}^{-1}$, which is ~ 3 times larger than that of the bulk CdS materials. The findings shed light on design of next-generation sensors and micro-electromechanical devices.

The technology on integration of flexible sensing electronics is very important for commercialization of health monitoring system. In fourth study, the non-standard (non-silicon technology) MEMS technology was developed for the fabrication of the integrated flexible sensing electronics. The technology is compatible to a kind of flexible substrates such as PET and PDMS. As an example, the modularized and integrated flexible sensor arrays were fabricated, which contains 9 pressure sensing units and a temperature sensing unit. The strong Van der Waals' force between two smooth PDMS substrate provides the flexible device with good stability and reproducibility. The results will pave the way for the practical application of flexible sensing devices in real-timely and simultaneously monitoring multiple physiological signals.

Acknowledgements

First and foremost, I would like to thank Prof. Liu Zheng for providing me the valuable opportunity to work on this interesting topic. His guidance and encouragement played an unprecedented role in shaping my research and the mode of thinking. His deep insight into several fields, incredible ability on finding the problems, and hardworking revision on my manuscript never ceased to amaze me. I deeply appreciate Prof. Liu for his supports and help not only in research but also in my daily life. Also, I am great proud to be his PhD student.

I also wish to express my deep appreciation to Prof. Zhang Ting of Suzhou Institute of Nano-tech and Nano-bionics of Chinese Academy of Sciences, for his continuous support and encouragement both in my research and life. Prof. Zhang acted as a beacon in my life, and always guided me in my most confused time.

I would like to thank all my friend and all group members. I have enjoyed working with them at NTU. I am thankful for the discussions with my friends, like Dr. Fu Wei, Dr. He Yongmin, Dr. Wang Hong, Mr. Liu Zhiyuan, Dr. Chen Bingbing, Dr. Gao Caitian, Mr Hu Hongwei, Assoc/Prof. Zhu Hongfei of Nanjing University, Prof. Zhao Wu of Northwest University. They are all excellent scientists.

I am grateful to the staff members of Nanyang Nano Fabrication Centre and FACTS for their equipment training and valuable suggestions in device fabrication and characterization.

Finally, I would like to dedicate this thesis to my parents and my wife Dr. Zheng Lu for their support on my study abroad.

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Abbreviations

CA	Carbon Array
CNT	Carbon Nantube
CNRs	Carbon Nanorods
CVD	Chemical Vapor Deposition
DART-PFM	Dual-frequency Resonance Tracking Piezoelectric Force Microscopy
ECGs	Electrocardiograms
EDS	Energy Dispersive X-ray Spectroscopy
EEGs	Electroencephalograms
EMGs	Electromyograms
EP	Electrophysiological
FEA	Finite Element Analysis
FETs	Field Effect Transistors
HRTEM	High Resolution Transmission Electron Microscopy
ICP	Intracranial Pressure
IOP	Intraocular Pressure
ISEs	Ion-Selective Electrodes
iSFET	Ion-Sensitive and Extended Gate Field-Effect Transistor
MEMS	Micro-Electro-Mechanical System
OLED	Organic Light-Emitting Diodes
OM	Optical Microscopy
PANI	Polydimethylsiloxane
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEO	Polyethylene Oxide
PEDOT: PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PFM	Piezoelectric Force Microscopy
PI	Polyaniline
PiI2T-Si	Polyisoindigobithiophene-siloxane

PL	Photoluminescence
PPy	Polypyrrole
PSR	Pressure Sensitive Resistance
PSC	Pressure Sensitive Capacitance
PU	Polyurethane
PZT	Lead Zirconate Titanate
P3HT	Poly(3-hexylthiophene)
RFID	Radio Frequency Identification
RIE	Reactive-Ion Etching
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
SKFM	Scanning Kelvin Force Microscopy
STFT	Short-Time Fourier Transform
TEM	Transmission Electron Microscopy
TCR	Temperature Coefficient of Resistance
TMDs	Transitional Metal Dichalcogenides
XRD	X-ray Diffraction

Chapter 1

Introduction

In this chapter, a brief introduction concerning the flexible sensing electronics and wearable health monitoring is stated followed by the introduction of the problems and challenges involved in the field of flexible sensors. Then, the answers on how to solve the problems, as well as the objective and scope of the thesis are emphasized. The organization of the dissertation is illustrated. Finally, the major findings and outcomes of this doctoral thesis are summarized.

1.1 Motivation and Significance

Hospital access of patient is required in the traditional centralized healthcare service. This is time-consuming and cannot address the patients' need timely, and it is dangerous for the persons who require emergency treatment. Conventional clinical practice is to employ the invasive detection such as Si-based rigid devices, and rigid multi-electrode pressure sensors for tracking physiological signals, however the use is yet rather limited because of the poor portability and wearability. For example, use of an implanted catheter with an external transducer is standard for monitoring intracranial pressure (ICP) in patients suffering from head trauma. The ability to continuously assess the pressure from the sole of feet is critical for treatment and prevention of plantar ulcerations for the diabetes patients [1-3]. However, conventional detection methods are costly and could bring discomfort for patients in clinical diagnoses and treatments. Also, the poor biocompatibility could cause infection and the second damage. To improve the comfortability, convenience, and security of health-monitoring in clinical diagnoses and daily life, the new concept of decentralized healthcare delivery was proposed and proofed: wearable and attachable health monitoring system (**Figure 1.1**) [4-6]. This novel smart system provides a convenient way to make healthcare (e.g. disease pre-diagnosis and health assessment) accessible to patients anywhere and anytime [7-8].

Figure 1.1 Wearable health monitors provide convenient way for portable healthcare, and promote the conventional diagnose method in clinical practice from centralized healthcare service towards decentralized healthcare delivery.

Wearable health monitoring system can be used to detect human physiological signals timely, which is an effective way for disease diagnoses and health assessments. Smart flexible sensing electronic is one of the crucial components in wearable health monitoring system. In the past years, various configurations of flexible sensors, including piezo-resistive, piezo-electrical, capacitive, and field effect transistor based devices, were designed in detection of tiny pressure and strain [9-16]. These sensors also were demonstrated the capability of high sensitivity for monitoring the human physiological signals such as heart rate, wrist pulse, and blood/intraocular pressure. The smart flexible sensing electronics can be used to track the health-related signals of human body, which will be analyzed the obtained information and compared with the standard clinical signals by wearable health monitoring system. In the case of improper signals, the wearable health monitoring system will alert the body conditions, and send the signals to doctors for further diagnoses and treatments. Real-time tracking physiological signals in sports is particularly important for a person to know amount of exercise and their body condition, while it is crucial for the person who suffers from the cardiovascular disease. In prospect, these flexible sensing devices could be used widely in the next wearable/portable health monitoring system for remote medicine.

1.2 Problem Statement

Currently, flexible sensing electronics are most exciting frontier for the next generation devices in both circuits and wearable/portable devices due to their unique properties, such as, strong stretchability and flexibility, which allowing the board to conform to any aspiring shapes for space saving. Also, the smart and multi-functionality broaden the place where electronic devices would be used. For example, these novel properties make the device could be used not only in wearable health-monitoring system and cost-effective disease diagnosis in telemedicine, but also in medicine robots and prosthetics (as shown in **Figure 1.2**). To meet those special characters and requirements, in past tens of years, inorganic nanowires and conducting polymer (including Si nanowires, Ag nanowires, SnO₂ nanowires, In₂O₃ nanowires, ZnO nanowires, InAs nanowires, and carbon nanotubes etc.) have been employed for constructing flexible electronics [17, 18, 22-28], both as electrodes

and as channel materials in field effect transistors (FETs). Although those achievements present valuable progress, many critical problems still existed, and limited their applications. For instance, inorganic nanowires cannot fulfil the requirements because of their intrinsic rigid and mechanical brittle properties; while semiconducting polymers present low carrier mobility, poor on-off ratio, and instability. Recently, two-dimensional (2D) materials including graphene, chemical modified graphene, h-BN, and transitional metal dichalcogenides (TMDs) were widely investigated and shown unprecedented performance in flexible sensing electronics with high-sensitivity, fast-response time and low power consumption etc [29-32]. Their exotic physical and chemical properties were demonstrated. **The advanced and novel nanostructured materials are the most promising materials for the next generation of flexible electronics, and need to be synthesized urgently. Their applications in health monitoring are also needed to be demonstrated.**

Low-cost and effective methods are urgently required for synthesis of programmable nanomaterials. As an example, graphene is considered to be a great candidate for the next generation of flexible/stretchable electronics [31, 33]. However, the practical application of graphene in flexible electronics is still limited because some bottlenecks have yet to be resolved. For example, the controllable micro-patterning of graphene at large scale, process compatibility with microelectronic manufacturing procedure, and low cost. Such fabrication process should be also compatible with the conventional microelectronic manufacturing procedure such as photolithography and printing electronic technology. In recent years, many efforts have been devoted to patterning graphene with microstructures and exploring its applications in flexible electronics. Three main strategies have been developed are: (i) guided growth on pre-patterned metal catalyst (Ni or Cu) [34-36]; (ii) post-patterning graphene film by reactive-ion etching (RIE) process [31, 32]; and (iii) printing electronic technology by graphene-based inks [37-40]. However, these methods have their disadvantages which largely limit their development toward practical applications. The method (i) needs high purity gas such as CH_4 for the synthesis of graphene, leading to high cost as well as the hazardous and inflammable condition. The method (ii) applied photoresist to graphene for RIE process where the residual organic

molecules cast shadows on graphene electrical properties. The highly-dispersed graphene inks were required in printing electronic technology (method iii). Typically, many defects could be induced by hydrophilic groups sitting on graphene and amphiphilic organic surfactant that were used to improve the dispersity and stability of graphene inks. As a result, the life time and performance of graphene ink based electronic devices need to be further improved. Also, the lateral resolution of less than 10 μm scale still challenging for printing electronic technology. Therefore, **new technology is now required for the controlled synthesis of patterned carbon materials like graphene.**

Micro-manufacturing technology put the electronic device towards smaller, smart, and less power consumption etc. Currently, micro-manufacturing technologies such as photolithography and electron beam lithography are widespread used in fabrication of microelectronic devices. There are many standard manufacturing parameters have been built for process of electronic device on rigid substrate such as silicon. The technologies are mature for traditional silicon based electronics. However, micro-manufacturing technology on flexible substrate is quite harder than that on rigid substrate due to its flexibility and mismatched mechanical properties between the substrate and conducting materials. Miniaturization and integration of flexible sensing devices are still challenging. Therefore, **the micro-manufacturing technology is required to be developed for integrated flexible sensor arrays.**

Flexible Sensing Electronics

- Prediction of early diseases
- Cost-effective disease diagnosis
- Wearable health monitoring
- Portable monitor for telemedicine
- Prosthetics

Figure 1.2 Flexible electronics and their applications

1.3 Objectives and Scope

This PhD project aims to develop the new method for synthesis of novel nanomaterials, and the new configuration and micro-manufacturing technology for the next generation wearable and flexible sensing electronics, which will be used in the portable personal health-monitoring system, and promote the applications of telemedicine. The project combines the fields in materials science and device physics with the specific aims for:

- (i) Synthesize and characterize the large-size, novel, and programmable nanomaterials, such as the novel conducting nanomaterials and semiconductors.
- (ii) Explore their growth process, and propose the growth mechanism by the chemical thermodynamics and growth kinetics.
- (iii) Investigate their fundamental physical and chemical properties, such as electrical transport and mechanical properties, and explain how the microstructures of materials make the contribution to their properties.
- (iv) Design the new type of healthcare devices by prepared novel nanomaterials, and explore applications in monitoring the health related human physiological signals, such as wrist pulse, heart rate, and body tremors.
- (v) Develop the micro-manufacturing technology for modularized flexible sensor arrays.

1.4 Dissertation Overview

Chapter 1 provides the motivation and significance of research on health-related flexible sensing electronics, and explains the problem statement on this field. Based on this motivation, the objective and scope of the thesis are established. Lastly, this chapter provides findings and outcomes of the entire thesis.

Chapter 2 reviews recent advances in flexible sensing electronics as well as their applications in wearable/attachable health monitoring devices. Firstly, in terms of system-level planning of theoretical and experimental strategies, various materials (polymers,

organic and inorganic nanomaterials etc.) used in construction of flexible sensing electronics with different types of configurations (piezo-resistive, piezo-electrical, capacitive, and field effect transistor based devices) are summarized. Secondly, the chapter also summarized the progress of flexible health monitoring sensors, such as artery pulse sensors, body temperature sensors, blood and sweat analysis sensors, EP sensors and IOP sensors. Finally, it also provides the questions to answer based on literatures.

Chapter 3 introduces the rationales for synthesis of materials including an explanation why carbon nanomaterials and CdS thin films were selected as target materials. The chapter discusses the principles underlying the synthesis, characterization techniques, and simulations employed as well as the methods of data analysis. The micro-manufacturing technologies for flexible sensing electronics are also summarized.

Chapter 4 presents our strategy for synthesis of programmable carbon nanomaterials. Inspired by the traditional photolithography process, the thesis developed a new method for synthesis of high crystallinity carbon patterns with wafer-scale and low cost. The method can produce the high crystallinity carbon patterns with a high lateral resolution of $\sim 2 \mu\text{m}$, which reaches the limitation of photolithography in contact mode. The chapter also demonstrated the materials' application in flexible sensing electronics for detection of bending and vibrations.

Chapter 5 presents our strategy for synthesis of self-crosslinked carbon nanorod arrays. This chapter developed the new type of carbon nanomaterials, 3-dimensional self-crosslinked carbon array (CA), where the individual unit is the intermediate state between the CNT and carbon nanofiber. Its applications in flexible sensing electronics were demonstrated. The unique nanostructures in the CA such as self-crosslinked points and vertically aligned nanorods reduced the residual stresses, making the CA-based flexible device possess high sensitivity and good stability ($\sim 10,000$ times) in the detection of flexions. As such, this chapter firstly demonstrated the CA-based flexible device's capabilities in monitoring the Parkinson's tremor for early diagnosis of Parkinson disease.

Chapter 6 describes the strategy for synthesis of CdS ultrathin films. In this chapter, ultrathin CdS thin films (~ 2 nm) were synthesized by chemical vapor deposition method. The giant vertical piezoelectricity of CdS in atomic scale (3~5 space lattices) has been demonstrated by in-situ SKFM, PFM and DART-PFM technology. The vertical piezoelectricity of d_{33} can be reaches to $d_{33}=32.8 \text{ pm}\cdot\text{V}^{-1}$, the 3 times larger than that of bulk CdS materials. This chapter also discussed their applications in sensors and actuators.

Chapter 7 presents the micro-manufacturing technologies for modularized and integrated flexible sensor arrays. In this chapter, the non-standard (non-silicon technology) MEMS technology was developed in the fabrication of smart and integrated flexible sensing electronics on a various kind of flexible plastic substrates such as PET and PDMS. A new modularized flexible sensor arrays which integrated 9 (3×3 array) pressure sensing units and body temperature sensor was proposed. The chapter also demonstrated the device possesses strong capability for monitoring health related physiological signals such as wrist pulse and body temperature.

Chapter 8 gives a summary of the new materials and technologies for the realization of health related flexible sensing electronics, and provides the recommendations for the future works from the materials view and technology view.

1.5 Findings and Outcomes

In this thesis, novel programmable nanomaterials such as high-crystallinity carbon patterns and self-crosslinked carbon arrays were firstly synthesized and applied in flexible sensing electronics. Their applications in flexible sensing electronics for health-monitoring have been demonstrated. The materials are new, and the main findings are summarized as follows:

- 1) Establishing method for controllable synthesis of programmable high crystallinity carbon pattern with the highest lateral resolution ($\sim 2 \text{ }\mu\text{m}$).
- 2) Demonstrating the bendable electronic devices by high crystallinity micro-patterned

carbon. These results will pave the way to next-generation carbon-based mechanical sensors.

- 3) Establishing new method for synthesis of 3D self-crosslinked carbon arrays and subsequently fabricated flexible sensing electronics for the detection of Parkinsonian tremors.
- 4) Finding self-crosslinked structure enhanced the contact points between individual carbon units and eradicated the electrical instability by reducing the residual stresses in the material. CA-based flexible sensors show high sensitivity and good stability ($\sim 10,000$ times) in the detection of flexions and low frequency vibrations (< 6 Hz), and are capable in monitoring the Parkinsonian tremor.
- 5) Developing the method for synthesis of ultra-thin CdS films (2-3 nm).
- 6) Discovery of the giant vertical piezoelectricity in atomic scale CdS thin films (3~5 space lattices), and firstly observing its vertical piezoelectric coefficient (d_{33}) of ~ 32.8 $\text{pm} \cdot \text{V}^{-1}$.
- 7) Establishing the non-standard micro-manufacturing technologies for fabrication of modularized flexible sensing electronics.

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Chapter 2*

Literature Review

This chapter summarizes recent advances in flexible sensing electronics as well as their applications in wearable/attachable health monitoring devices. In terms of system-level planning of theoretical and experimental strategies, various materials (polymers, organic and inorganic nanomaterials etc.) used in construction of flexible sensing electronics with different types of configurations (piezo-resistive, piezo-electrical, capacitive, and field effect transistor based devices) have been reported. The chapter also summarized the progress of flexible health monitoring sensors, such as artery pulse sensors, body temperature sensors, blood and sweat analysis sensors, EP sensors and IOP sensors, all of which may be used in wearable/portable personal health-monitoring systems and promote the applications of telemedicine.

*This section has been published substantially as: “**Xuewen Wang**, Zheng Liu, Ting Zhang, Flexible Sensing Electronics for Wearable/attachable Health Monitoring” *Small*, **2017**, 1602790.”

2.1 Strategies towards Flexible/stretchable Sensing Electronics

Flexible and stretchable sensing electronics for wearable health monitoring are complex integrated systems, which typically compose of (1) flexible/stretchable substrates, (2) conducting electrodes, (3) sensing materials, and (4) occasionally, encapsulation materials. [1-21] As such, attention should be paid to the individual roles of each component, their interactions, and how these interactions affect the performance of the system. To achieve mechanical flexibility and stretchability, mostly two approaches on material science and engineering have been employed: elastic materials and stretchable/flexible structures (as shown in **Figure 2.1**). Being intrinsically flexible/stretchable materials, elastic films, liquid metal, ionic liquid, conducting polymers and organic semiconductors have been used and investigated in flexible electronics. [22-25] However, these materials usually present low mobility as sensing channels in FET devices, and display instability when exposed to light for a sustained period of time. Another important strategy for stretchability is to design materials integrated with special structures, such as serpentine, helix and other micro/nanostructures. Previous research has demonstrated that inorganic nanomaterials can become flexible when their size and thickness are reduced to 100 nm.[26-28] Structure engineering such as fabricating wavy ribbons and twisted-pair lines make the device stretchable and flexible, which is the same concept as an accordion that can be stretched through its wavy design (Figure 2b).[29] The fabrication process for wavy ribbon structures usually starts from the flat ribbon chemically bonded to a pre-strained compliant substrate. When the strain is released, the ribbon will be compressed to generate a wavy layout through a nonlinear buckling response.[30] This wavy layout can accommodate external deformations through changes in wavelength and amplitude (Figure 2c).[31] Besides shape deformation, the electrode and sensing materials also need to have stable electrical performance when suffering large and reversible deformation.

Figure 2.1 The typical strategies and conducting materials towards mechanical flexible. (a) The main intrinsic flexible and stretchable materials for flexible devices. The electrical insulated polymer such as PDMS, PI, PET and PEN can be used as the substrate; (b) geometry design of inorganic materials could produce stable electric output when materials such as Si wavy structure (c) and network films (d, e, f, and g) of Ag nanowire, Au nanowire, Cu nanowire (c-e) suffer large deformations, scale bar is 500 nm for e. Reproduced with permission.[73] Copyright 2013, Nature Publishing Group.

2.1.1 Flexible Substrates

Substrate material plays a huge role in the device construction. Typically, flexible polymers, rubbers, and metal foils are widely used as substrates due to their thermal stability, good chemical resistance, and great mechanical flexibility. Their chemical and physical properties are summarized in **Table 2.1**. Amongst polymer substrates, polyimide (PI) exhibits great flexibility, very low creep and high tensile strength, all of which can be maintained during continuous use at temperatures up to 452 °C.[32, 33] It also resists weak acids and alkalis, as well as commonly used organic solvents, e.g., ethanol and acetone. These properties make PI compatible with the manufacturing processes of Micro-Electro-

Mechanical System (MEMS). Several groups have fabricated various flexible pressure sensing matrices on PI substrates and have demonstrated small bending radii of 100 mm for organic transistors and pressure sensors on very thin (12.5 μm -thick) PI substrates.[34] However, the yellow colored material makes such devices have low transparencies. Special applications need a substrate to have high transparency and low birefringence, such as a system integrated with flexible transparent display and solar cell. In contrast, polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) are optically clear with transmittance of >85% in the visible wavelength region.[35, 36] However, they are thermally less stable than PI, and can also be easily permeated by oxygen and water (water absorption of ~0.14%) and present poor stretchability due to their relatively high modulus of elasticity (~2-3 GPa). Recently, self-healing materials were developed for stretchable electronics.[37-39] The materials enable the device to heal itself when mechanical damaged. This feature can be used to design the new type of flexible devices that to mimic the self-repair capability of human skin.

Table 2.1 Summary of the typical flexible substrates and their chemical and physical properties.

Materials	Stretchable/bendable	Transparency/ Dielectric constant	Thermal stability/ Coefficient of thermal expansion	Chemical Resistance	Reference
PI	Bendable	Low transparency (yellow color) 2.8-3.5	Resist temperature (<450 °C) $\sim 5 \times 10^{-5}/\text{K}$	Weak acids and alkali Ethanol and acetone	[10, 12, 32-34, 163, 176, 192, 198]
PET	Bendable	High transparency (>85%) 2.5-3.5	Resist temperature (<100 °C) $\sim 7 \times 10^{-5}/\text{K}$	Dissolvable in acetone	[35, 89, 182, 184]
PEN	Bendable	High transparency (>85%) 2.9-3.2	Resist temperature (<180 °C) $\sim 2 \times 10^{-5}/\text{K}$	Easily permeated by oxygen and water	[36, 178]
Silicone (PDMS, Ecoflex)	Stretchable	High transparency (>95%) 2.3-2.8	Resist temperature (<100 °C) Thermal expansion $\sim 30 \times 10^{-5}/\text{K}$	Ethanol and acetone (in short time)	[9, 46-60, 116, 195]
Metal foil	Bendable	No Good conductivity	Resist temperature (~250 °C) Thermal stable	Ethanol and acetone Moisture and oxygen	[220, 221]
Paper	Bendable	No 2.3-3.0	Resist temperature (<100 °C)	No	[222, 223]

Self-healing	Stretchable	Low transparency (92%) Ionic conductivity	Thermal healing Thermal expansion	Moisture and oxygen Ethanol and acetone (in short time)	[37-39]
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The fiber and textiles are highly desirable for wearable electronics because the textiles are the most natural materials close to human skin, and were considered to be the second human skin. By integration with multifunctional electronics, the novel textiles possess both functionalities of flexible electronics and the features of clothing-like textiles. There are mainly two ways to realize the textile-based flexible electronics: the textile was integrated with traditional and small rigid sensors, and textile that composed by conducting and sensing fiber for sensor configuration.[40, 41] Up to now, various smart textiles were developed for sensing the environmental conditions and health related physiological signals.[42-44] For example, the conductive yarns can be wove into fabric for smart textiles, which were equipped with multifunctional sensors, and showed the capability in monitoring the electrocardiograph (ECG) signals and blood pressure.[45] Therefore, the textile provides a valuable platform for wearable devices that bring traditional textile towards multi-functionality and smart.

The wearable devices require durable and compatible substrates for various application scenarios. For instance, the biocompatible materials need to be used for medical devices, which can be attached to the human body without causing an infection. Recently, polydimethylsiloxane (PDMS) has been widely used as a substrate material in flexible/stretchable devices due to its biocompatibility and intrinsic high stretchability (~100%-1100%). To improve the adhesion between the PDMS substrate and attached components, various surface treatment technologies including oxygen plasma, ultraviolet exposure, and chemical functionalization have been employed to modify its hydrophobic surface to become hydrophilic.[46-52]

Figure 2.2 Fabrication of micro-patterned PDMS films a) Schematic of the fabrication process for micro-patterned PDMS films; b) SEM images of the patterned PDMS films with the structure of hemispheres, pyramids, microrods, microlines, cubic features, and pyramid features; Reproduced with permission.[53] Copyright 2010, Nature Publishing Group; Reproduced with permission.[54] Copyright 2012, American Chemical Society; c) Silk-mold and prepared micro-patterned PDMS film. (c) Reproduced with permission.[9] Copyright 2014, Wiley-VCH.

The microstructured PDMS film is considered to be the most popular flexible substrate to integrate sensitive nanomaterials for the flexible sensors due to its excellent elasticity and biocompatibility. Creating microstructures on PDMS film can not only enhance the stretchability, but also endow the flexible sensing device with higher sensitivity and faster response time than unstructured PDMS thin films.[53-58] During a typical fabrication process (**Figure 2.2a**), a micro-patterned mould was first prepared by MEMS technology (spin coating, lithography, and etching etc.), and the PDMS mixture of base and cross-linker ($v_{\text{base}}:v_{\text{cross-linker}}=10:1$) was stirred and degassed in vacuum to get rid of bubbles.

Then, the PDMS mixture was spin-coated onto the mould, solidified, and peeled off from the mould to get microstructured PDMS film. As show in Figure 2.2b, various microstructures including hemispheres, pyramids, microrods, and microlines were prepared by this method. Also, a bio-inspired strategy was developed to fabricate PDMS films with micro-/nano-structures molded by plant leaf, but this method is not a controllable process for making microstructured PDMS films with desired density and size.[59, 60] Recently, we proposed a simple and low-cost method for fabrication of large-area micro-patterned PDMS films with uniformed microstructures (Figure 2.2c).[9] We found that high-quality textile made of silk, possessing microstructured surface intertextures, can act as effective moulds for the construction of patterned flexible PDMS thin films. The aspect ratios of patterned films can be well controlled by changing the ratio of horizontal and vertical lines on the textile mould. In our work, the mould we chose has the crisscross pattern, which is the most popular structure used for textiles. The versatile textile moulds provide many template options for controllable fabrication of flexible micro-patterned films with low cost and luxuriant micro-structures. The method also can produce anisotropic microstructures on PDMS substrate, which will be beneficial for smart flexible transducers that can detect pressure directions. Novel and more advanced substrate materials with special features are still desired for flexible devices. An example is self-healing materials that can endow devices with the self-healing capability when they are mechanical broken.[38, 61] Another example is bio-degradable materials or self-degradable materials such as wood and paper that can minimize the electronic waste (e-waste) for the next generation of flexible electronics.[62]

2.1.2 Flexible Conducting Electrodes and Sensing Materials

Both conducting electrodes and sensing materials are crucial components that can be embedded in or on the top of elastic substrates for flexible devices. Traditional materials such as Au, Pt, and indium tin oxide (ITO) films have been demonstrated in the construction of high sensitivity flexible sensors as electrode materials. However, their rigid and brittle mechanical properties lead to cracks during deformation, which limit their applications in flexible/stretchable devices. Nanowire and nanotube networks were

considered to be the most promising substitutions to replace these rigid materials due to their transparent, stretchable, electrical stable, and durable properties.

The network structure of interconnected nanowires or nanotubes provides an effective path for electrons with their high optical transparency. Over past decade, metal nanowires (e.g., Ag, Cu, and Au) were widely investigated and employed as electrode materials for the construction of flexible/stretchable devices (Figure 2.1d-g), where the sheet resistances were controlled within the range of $\sim 3 \Omega \text{ sq}^{-1}$ to $500 \Omega \text{ sq}^{-1}$, and the transmittances ranged from $\sim 70\%$ to $\sim 97.3\%$. [63-65] For example, the flexible transparent conducting electrode fabricated by the co-assembled Ag/Te nanowires showed an average transmittance up to 97.3% for the best transmitting network, and sheet resistance was as low as $2.7 \Omega \text{ sq}^{-1}$, which exhibited better performance than a 80 nm thick layer of ITO sputtered on glass. [66] In fact, electrical and optical properties largely depend on the nanowire's diameter, length, and number density. [67] Previous reports have demonstrated that the network of nanowires with high aspect ratios (length/diameter) presented higher conductivity and transparency than that with low aspect ratios. [68] A network of nanowires with high aspect ratios has a reduced number of contact resistances, allowing electrons to traverse much farther across a network film without encountering the high resistance of the nanowire contacts. However, the contact resistance at the interface between the nanowires still casts a shadow on the electrical stability when bending. To eliminate the negative influence from contact resistance, scientists reduced the contact points and contact resistance by aligning and welding the nanowires of network films. [66, 69-72] However, new methods and technologies still need to be developed because the method of welding nanowires is only applicable for specific materials.

Other approaches to reduce the contact resistance between nanowires include the construction of conductive networks by sputtering and physical deposition with various templates. Recently, Wu et al. present a facile method for fabrication of metal nanotrough network structures based on the polymer nanofibers template. [73] As transparent conducting electrodes, these metal nanotrough exhibit both excellent optoelectronic performance (sheet resistance of $\sim 2 \Omega \text{ sq}^{-1}$ at 90% transmission) and remarkable

mechanical properties (to tolerate large bending and stretching stresses). Guo et al. demonstrated highly stretchable and transparent Au nanomesh electrodes on elastomers by grain boundary lithography.[74] The change in sheet resistance of Au nanomeshes was modest with a one-time strain of $\sim 160\%$ (from $\sim 21 \Omega \text{ sq}^{-1}$ to $\sim 67 \Omega \text{ sq}^{-1}$), or after 1,000 cycles at a strain of 50%. In addition, bio-inspired networks including extracted leaf venation and metalizing a spider's silk web have been demonstrated with exceptional optoelectronic and mechanical performances in flexible electronic applications.[75] These metal nanomesh, nanotrough, and network electrodes look promising in replacing rigid metal films in many applications such as solar cells, touch screen, flat panel displays, and flexible/stretchable sensors.

Semiconducting polymers and nanowires have been demonstrated as promising sensing materials in flexible electronics applications. Polymers including polyaniline (PANI), polypyrrole (PPy), poly(3-hexylthiophene) (P3HT) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), have been employed for constructing flexible electronics such as channel materials in field effect transistors (FETs).[76-79] However, their electronic performance presents low carrier mobility and instability, which are not comparable with inorganic semiconductors such as the nanowires of SnO_2 , In_2O_3 , ZnO and InAs , as well as carbon nanotubes.[80, 81] Despite these drawbacks, polymers are attractive in terms of their highly tunable chemical and physical properties, which can be controlled by altering their components and molecular structures. An attractive feature of semiconducting polymers is that their mechanical properties are close to that of most insulated polymer substrates, which make them ideal candidates for integration with polymer substrates. Additionally, their Young's modulus is smaller than that of inorganic nanowires, which is comparable to human skin (0.34 MPa).[82] This particular property provides the material with the capacity for implementation in attachable and wearable electronic applications for human skin. For example, through the multiphase reaction of PPy hydrogel, Pan et al. synthesized hollow-sphere structures of PPy for reducing the elasticity and Young's modulus. They also demonstrated ultrasensitive resistive pressure sensors based on such microstructured PPy.[79] By combining a microstructured PDMS dielectric with the high-mobility semiconducting

polyisobithiophene-siloxane (PiBT-Si) in a monolithic transistor, Schwartz et al. reported flexible pressure-sensitive organic thin film transistors with maximum sensitivity of 8.4 kPa^{-1} , a fast response time ($<10 \text{ ms}$), high stability over 415,000 cycles, and a low power consumption ($<1 \text{ mW}$). [8] The author also demonstrated the applications of such a device in the continuous monitoring of radial artery pulse wave. Although these progresses present the valuable advances of semiconducting polymers, several drawbacks still exist that narrow their applications in flexible/stretchable devices. Most semiconducting polymers cannot work for long time under applied force or strain, due to their mechanical aging problem.

Carbon-based nanomaterials including carbon nanotube (CNT) and graphene have proven unprecedented performance in flexible electronics due to their excellent chemical and physical properties (e.g., high optical transmittance of their thin films, remarkable mechanical flexibility, and tunable metallic/semiconducting properties of CNT). [83-85] Over past few years, much effort has been devoted to fabricate CNT/polymer composites for stretchable conductors. [78, 86-90] For example, the composites of CNT and PDMS were widely employed to fabricate pressure-sensitive rubbers for piezo-resistance pressure sensors. [91-94] The porous structures in composites have been considered an effective way to increase the sensitivity of pressure-sensitive rubbers, where the Young's modulus decreases and brings about large deformation under a tiny applied force. Jung et al. synthesized porous pressure-sensitive rubbers based on CNTs by using reverse micelles to introduce pores into conventional rubbers. [95] The pore characteristics and system modulus can be readily controlled by the components. The author also demonstrated pressure sensors, strain gauges, and the wearable multi-channel human-machine-interface devices for the wireless control of robots. However, the CNT/polymer composites are opaque.

Recently, we demonstrated transparent and ultra-sensitive pressure sensors with single-walled carbon nanotube (SWNT) ultrathin films and flexible non-contact humidity sensing devices by reduced graphene (rGO) ultrathin films on plastic substrates. [9, 96, 97] We established a facile and reproducible layer-by-layer exfoliation method to assemble SWNT

films with ultrathin thickness (~20 nm), high transparency (~95% at 550 nm), wafer scale fabrication capabilities, and tunable sheet resistance.[96] The obtained free-standing ultrathin films exhibit structure homogeneity and uniform electric conductivity, and the thickness of the rGO ultrathin films can be precisely controlled by using solvents with different surface tension. Based on these materials, we have also showcased flexible sensing devices, and their applications in monitoring the physiological signals for health assessment. The flexible device presents the capability of monitoring human physiological signals such as wrist pulse and throat muscle movement when a person is speaking, which may broaden its potential applications for disease diagnosis and voice recognition.[9]

2.1.3 Device Configurations

Piezoelectric/Piezo-resistive type pressure/strain sensors. The principle of piezoelectric type pressure/strain sensors is based on piezoelectricity, where electrical charges are generated when external pressure/strain is applied to the piezoelectric materials. This electromechanical interaction only occurs in certain types of materials that have non-centrosymmetric crystal structures. Piezoelectricity is instantaneously generated when the materials are under strain and pressure. Therefore, piezoelectric type pressure/strain sensors possess ultrafast response time and high sensitivity. Popular piezoelectric materials, ZnO nanowires and lead-containing materials like lead zirconate titanate (PZT) were widely investigated for the construction of flexible pressure sensors due to the high piezoelectric constants characteristic of the asymmetric crystal structures of hexagonal ZnO nanowires and PZT (**Figure 2.3a, b, e**).[80, 81, 98-102] However, the usage of inorganic materials shows disadvantages such as high cost manufacturing process and high toxicity of lead-containing materials. Also, the flexibility of such inorganic materials was not comparable to organic materials and polymers, and this eventually limited the applications due to their small dynamic response range. Polymer based piezoelectric materials like PVDF and the composites of polymer and inorganic piezoelectric materials, have attracted increasing interest due to their mechanical flexibility and cost-effective processing technology.[103, 104] These materials make use of the mechanical flexibility of polymers and the high performance of piezoelectric inorganics, and therefore are far

more superior to rigid materials in certain applications.

Figure 2.3 Piezoelectric and Piezo-resistance type pressure sensors. a) Schematic and b) photograph of piezoelectric material (vertical ZnO nanowire) based flexible pressure sensor; c) Schematics and d) photograph of piezo-resistance type flexible sensor constructed on micro-patterned PDMS substrate, the scale bar is 1 cm for d; (c) Reproduced with permission.[92] Copyright 2014, American Chemical Society; (d) Reproduced with permission.[55] Copyright 2012, Nature Publishing Group; e) I-t response curve of piezoelectric pressure sensor with varying applied pressures; (a, b, e) Reproduced with permission.[145] Copyright 2013, AAAS; f) I-t response curve of piezo-resistance pressure sensors for detection of tiny pressure.

Piezo-resistivity is the most common characteristics for pressure/strain sensors. There are mainly two key parameters to effectively realize the piezo-resistive effect: (i) soft and flexible substrate, and (ii) special micro/nano-structures of the conductive sensing materials. It is widely accepted that the mechanical hysteresis of polymers will lead to imperfect performances of flexible pressure/strain sensors with the long response and recovery times. Conductive materials have special structures that enable the polymer matrix deform upon being compressed by the pressure. Such deformations will provide electrons with more percolating channels and cause an increase in conductivity (Figure 2.3c and d). With the advancements of novel nanostructured materials, 1-dimensional carbon nanotube,[92, 105-108] Ag nanowire,[109-115] Au nanowire,[116] 2-dimensional graphene,[117-123] 3-dimensional graphene foam[124-127] and polymer/inorganic composite[56, 95, 128, 129] were developed to prepare flexible sensors as conductive sensing materials. These materials exhibit great performances with features such as high sensitivity, fast response/recovery time, low detection limit, as well as high repeatability and durability (Figure 2.3f). Moreover, the low working voltage and energy consumption make resistive-type devices the ideal candidates for wearable/portable electronic system.

Capacitive type pressure/strain sensors. Flexible capacitive-type sensor is one of the most important devices in sensing pressure and strain. A typical capacitor is constructed by two parallel electrodes sandwiched a dielectric layer (**Figure 2.4a**). The capacitance (C) of this parallel-plate capacitor is given by the following equation:

$$C = \epsilon \cdot S / d$$

where ϵ denotes the permittivity of the dielectric layer. S and d are the effective area and distance between the top electrode and bottom electrode, respectively. Normally, when a force is applied to a flexible device, it causes elastic deformation, which may change the value of S and d, and ultimately result in the change of capacitance (Figure 2.4a). Over past several years, Au films have been used as the top and bottom electrodes to construct flexible capacitive sensing devices.[130-132] However, several research work have pointed out that metal layers on PDMS are prone to cracks. The interface properties between the substrates such as PDMS and the Au conducting layer are critical. Recently, it was reported that carbon nanotubes and Ag nanowire networks were embedded in PDMS

for elastic conducting films, and the carbon nanotube network can be stretched up to 700% with the corresponding significantly increased resistance.[53, 110, 114, 115, 133-135] Prof. Zhenan Bao and co-authors from Stanford University reported that flexible capacitive-type pressure and strain sensors based on carbon nanotubes on PDMS possessed good performance (the linear response for pressure from 0 to 1 MPa, as shown in Figure 2.4b-g). They prepared transparent and conducting spring-like single-walled carbon nanotube films on PDMS substrate, which accommodated strains up to 150% with conductivity as high as $2200 \text{ S} \cdot \text{cm}^{-1}$. [46] In addition, a highly sensitive pressure sensor can be achieved by changing the dielectric layers using different materials and structures. For example, micro-structured PDMS dielectric layer can dramatically increase the sensitivity of sensors, and this unprecedented improve in performance is caused by the air voids in the PDMS dielectric layers, which has a lower dielectric constant ($\epsilon = 1.0$) than PDMS ($\epsilon \sim 3.0$). [9, 54, 136] Also, it was declared that the combination of textile electrode and multi-layer dielectric such as air gap and fluorosilicone can produce exceptional results for three-axis flexible pressure sensors with high compliance, robustness and stability under manipulation.[57] Moreover, an elastomeric foam with microcellular structures was implemented for flexible pressure sensors as the carrier and the sensitive material, and showed high deformability and reliable performance for capacitive pressure sensors.[137] Simple configurations and fabrication, as well as the stable and durable performance are important features for capacitive sensors (Figure 2.4h).

Figure 2.4 Capacitive flexible sensors. a) Schematic showing a stretchable capacitor after being placed under pressure (left) and being stretched (right); b, c, and e, f) Performance of capacitive flexible sensor in the detection of pressure and strain; d, g) Photograph of capacitive flexible sensor arrays and corresponding capacitance change for pressure mapping; Reproduced with permission, the scale bar is 2 mm.[46] Copyright 2011, Nature Publishing Group; h) Au film based capacitive pressure sensors, the device can sustain crumpling and sharp indentation. Reproduced with permission.[137] Copyright 2013, Institute of Physics;

FETs based flexible pressure/strain sensors. The FET based sensor can be implemented by setting the pressure sensitive resistance (PSR) onto its source (**Figure 2.5a:i** and **b**), drain (**Figure 2.5a:ii, d** and **e**) and gate, or through using the pressure sensitive capacitance (PSC) instead of a dielectric layer in between the gate and channel material (**Figure 2.5a:iv** and **c**). In 2004, a FET based flexible pressure sensor was reported and named as “electronic skin” for the first time.[138] This device was constructed using organic semiconductor film as channel materials.[36, 139] Typically, a sensitive skin consists of thousands of pressure sensors, which would require a flexible switching matrix that cannot be realized with present silicon-based electronics. Organic FETs can achieve this purpose not only through their inherent flexibility and potential low cost for a large areas, but also through simple manufacture processes for integration of large areas, such as ink-jet printing technology and aerosol-jet printing technology.[140] In the following years, multifunctional features of FETs type sensors, such as a combination of pressure and temperature sensor[141] as well as pressure sensor and organic light-emitting diodes (OLED)/nanowire based LED,[142] have been demonstrated using pentacene, silicon nanowires,[143, 144] vertical ZnO nanowires[145, 146] and carbon nanotubes as the channel materials (**Figure 2.5**).[140, 147, 148] Multifunctional electronics represent a new approach to flexible consumer electronics by optical and mechanical means, with potential applications in human-machine interaction, touch screen, robotics, optical microelectron-mechanical and medical/health monitoring systems. However, the high working gate voltage confines their applications in wearable/attachable electrical systems. Also, toxicological properties of organic semiconductors limit their applications in intrusive medical examinations such as surgical gloves and cardiac ablation therapy. In general, FETs-typed flexible pressure/strain sensors tend to be more sensitive than resistive and capacitive type devices because of their capacity to tune the conductance of semiconducting channel materials by controlling the gate voltage. These features make FETs based devices the ideal candidates for flexible electronic sensing devices, although these types of devices require slightly more complex manufacturing processes and supplementary electronics than resistive and capacitive ones.

Figure 2.5 FETs based flexible pressure sensors. a) Schematic for different type of FETs based pressure sensors; b) Source controlled and nanowires based FET pressure sensor arrays; Reproduced with permission.[143] Copyright 2010, Nature Publishing Group; c) Schematic of gate and capacitive controlled FET pressure sensor; Reproduced with permission.[8] Copyright 2013, Nature Publishing Group; d, e) Drain controlled FET pressure sensor array and its performance in mapping the pressure from the metallic ring; Reproduced with permission.[36] Copyright 2013, Nature Publishing Group; f) Schematic of piezo-phototronic effect based pressure sensor for imaging pressure distribution. Reproduced with permission.[142] Copyright 2013, Nature Publishing Group;

2.2 Flexible Sensors for Monitoring Physiological Signals

2.2.1 Blood and Sweat Analysis

The blood sugar concentration or blood glucose level is an important indicator of certain diseases such as diabetes mellitus. Currently, the most widely used method is “finger-pricking” for blood sampling and this is followed by analysis in a portable glucose meter. However, this method is inconvenient and there is the risk of infection during blood sampling process. Enzyme-based microneedle sensors provide us with a minimally invasive sensing method, which requires the device to be inserted into the skin to measure the glucose levels in the skin interstitial fluid. The blood glucose level can be calculated from the correlation between glucose levels in the skin interstitial fluid and in the blood.[149-151] However, this method cannot allow for a completely non-invasive monitoring.

Flexible and wearable sensing devices have been proven to be convenient, real-time, and safe for detection of glucose levels, through the analysis of sweat and tears. For example, Kudo et al. reported a flexible and wearable glucose biosensor produced by soft-MEMS technology.[152] A hydrophobic PDMS membrane, hydrophilic co-polymer membrane and film electrodes of Pt and Au were used for constructing the sensor. The sensor showed high flexibility and good performance when it encountered a 120% expanding deformation, and possessed high sensitivity and linear output to glucose levels in the range of 0.06–2.00 mmol/L. Recently, Bandodkar et al. demonstrated a fully-printed tattoo-based wearable electrochemical biosensor for noninvasive glucose monitoring with the detection limit at micro-molar levels.[153, 154] It is the first example of an easy-to-wear flexible tattoo-based epidermal diagnostic device combining reverse iontophoretic extraction of interstitial glucose and an enzyme-based amperometric biosensor (**Figure 2.6a**). Correlation of the sensor response with that of a commercial glucose meter underscores the potential of the tattoo-based sensor to detect glucose levels noninvasively. Besides the methods mentioned above, the smart contact lens from Google bring noninvasive blood

glucose monitoring for diabetics through the measurement of the tears.[155] This device comprises of a lens made of common lens hydrogel material embedded with a tiny wireless chip, a miniaturized glucose sensor and a tiny battery between two layers in the periphery of the lens (Figure 2.6b).

Figure 2.6 Flexible sensing devices on blood and sweat analysis. a) All-printed tattoo-based glucose sensor for noninvasive monitoring glycemic level; Reproduced with permission.[129] Copyright 2015, American Chemical Society; b) Google smart lens for noninvasive blood glucose monitoring by detection of the tear fluid; Reproduced with permission.[130] Copyright 2014, Nature Publishing Group; c) The wireless capacitive attachable sensor designed for sensing specific ions (OH^- , H^+ , Cu^+ , and Fe^{2+}) of sweat from the surface of the skin; Reproduced with permission.[169] Copyright 2015, Wiley-VCH; d, e) Schematic and photograph of electrochemical sensor array for simultaneous

monitoring of the multiple informative biomarkers from sweat; f) System-level interference studies of the sensor array. Reproduced with permission.[6] Copyright 2016, Nature Publishing Group;

pH value is another important parameter to evaluate body condition as it strongly correlates with the wound healing in human skin. In recent years, several methods have been developed for sensing pH value, including ion-sensitive and extended gate field-effect transistor (iSFET) based pH sensors, optical fiber based pH sensors, and hydrogel film based pH sensors.[156-161] Electrochemical sensors made by polymer (PANI, PVB) and inorganic nanomaterials (ZnO , IrO_x , WO_3) have also demonstrated their capabilities in sensing pH value.[153, 162, 163] Joseph Wang's group reported pH-sensitive bandages that directly attach to the human body for pH sensing. The device presented a Nernstian sensitivity over the 4.35–8.00 pH range.[164] The same group also developed novel tattoo-based, solid-contact ion-selective electrodes for non-invasive potentiometric monitoring of epidermal pH.[153] They employed the pH-sensitive conducting polymer of PANI associated with carbon as active materials to construct potentiometric sensors. The device was applied to the lower back, neck and wrist of human body and evaluated for real-time measurement of pH levels of human perspiration during exercise, and displayed rapid and sensitive response to a wide range of pH changes. Curto et al. reported a wearable chemical barcode optical sensing device, which was able to respond to pH changes by employing a pH-sensitive dye.[165] The advantage of this device is that it does not contain conventional electrodes, avoiding the risk of an electric shock in vivo applications.

In addition, the flexible sensor arrays that integrate with the multiple wearable electrochemical sensors can be used to simultaneously monitor multiple informative biomarkers in sweat secretion, such as glucose, lactate, sodium ions, and potassium ions.[6, 166] The measurement of glucose and lactate can be achieved by enzymatic sensors, which equip glucose oxidase and lactate oxidase on a permeable film as working electrodes, coupled with a shared reference electrode of Ag/AgCl. The concentrations of Na^+ , K^+ , and Ca^{2+} can be measured through the working electrode of ion-selective electrodes (ISEs) with a Ag/AgCl reference electrode (**Figure 2.6c-f**). The wearable sensor arrays could be

exploited for real-time tracking of multiple biomarkers in sweat and other body fluid.

2.2.2 Wrist Pulse and Heart Rate Tracking

In clinical practice, artery pulse is a significant indicator of arterial blood pressure, heart rate, and aged or stiff blood vessel. It provides useful information on a possible cardiovascular disease through non-invasive medical diagnosis.[167, 168] For example, cardiovascular disease such as atherosclerosis is asymptomatic in the very early stages, but it leads to arterial pulse pathologic, affecting arterial blood pressure, and resulting in a change of the wrist pulse waveform. Therefore, continuous monitoring of the wrist pulse is a rapid and noninvasive method for diagnosing a cardiovascular disease. Typically, a wrist pulse waveform contains three main waves: percussion wave (P-wave), tidal wave (T-wave), and diastolic wave (D-wave) (**Figure 2.7e**), where P-wave is the early systolic peak pressure, T-wave is the late systolic peak pressure and D-wave appears in the diastole region and is referred to as the diastolic pulse waveform.[167, 169, 170] The waveform is formed by the blood pressure from left ventricle contracts and reflect wave from the lower limb. Clinically significant parameters can be extracted from these peaks. For example, P-wave/T-wave is defined as the radial artery augmentation index (AIr) and the time delay between the P-wave and T-wave peaks is defined as ΔT_{DVP} . [171-173] These two parameters represent the arterial stiffness level, which is highly related to a person's age and the health condition. Conventional strategies for monitoring artery pulse include using infrared based photo-electric devices or rigid multi-electrode pressure sensors. However, these devices are costly and can cause discomfort compared with flexible electronics. Flexible/attachable devices pave the way for the next wearable/portable wrist pulse health continuous monitoring system.

Up to now, various materials have been employed to fabricate flexible/attachable devices for monitoring wrist pulse including ZnO-based flexible fibers, Pt-coated nanofibers, CNT films, Au nanowires, CNT/PDMS composite, semiconducting polymers, PZT and PVDF films, and metal-organic frameworks.[9, 10, 55, 93, 116, 174-181] For example, Pt-coated nanofibers based devices and ZnO-based flexible fiber generator can be used for real-time

monitoring of the heartbeat when attached to the artery of the wrist, but more detailed information related to body health (P-wave, T-wave, and D-wave) cannot be obtained due to their limited sensitivity (Figure 2.7a and b). We reported ultrasensitive flexible electronic skins by combining micro-patterned PDMS and single-walled CNTs film, and demonstrated their applications in real-time monitoring of wrist pulse (Figure 2.7c).[9] Our devices can clearly identify the subtle differences in blood pulses, and we can observe the characteristic pulse waveform shape with three typical distinct waves (Figure 8d and e). The pulse signals of our electronic skin devices were compared with those of high-accuracy capacitive tactile pressure sensors (PPS's pulse Tact System from Pressure Profile Systems, Inc. USA). Hundreds of wrist pulse cycles of a healthy person were collected by the electronic skin, and the results were well-matched with that from PPS sensors, all of which clearly indicates that the flexible electronic skin device presents an accurate measurement for monitoring wrist pulse.

Figure 2.7 Flexible pressure sensors for real-time monitoring of the artery pulse. a, b) Schematic illustration to detect pulse on a human's neck with pressure sensor and its performance; Reproduced with permission.[11] Copyright 2015, Wiley-VCH; c, d, e) Flexible piezo-resistive pressure sensor for tracking the wrist artery pulse; Reproduced with permission.[9] Copyright 2014, Wiley-VCH; f) Schematic of a wearable e-skin for monitoring artery pulse pressure and temperature; g, h) Real-time I-t curves of e-skin on monitoring the wrist pulse at different temperatures. Reproduced with permission.[189] Copyright 2015, AAAS

As a pioneer in the field of electronic skin research, Zhenan Bao's group at Stanford presented great results with flexible polymer transistors, which were able to detect small features in the diastolic tail of the pulse pressure wave that most sensors used in arterial

tonometry cannot detect.[8] They showcased sensors with low power consumption (<1 mW), which is crucial for wearable electronics that require prolonged battery duration. Recently, they demonstrated the most miniaturized monitoring devices (millimetre-scale sensors) to wirelessly measure real-time wrist pulse waveforms.[12] Compared with wired devices, these small wireless devices could impose fewer constraints on body movements, and the output of the sensor signal could be more stable during movements. It is anticipated that this new concept of wireless monitoring technology can be scaled up for continuous detection of other physiological signals in clinical medicine.

To improve the wearability of flexible monitoring devices, Dagdeviren et al. reported lead zirconate titanate (PZT) ultrathin film based electronic tattoo devices.[10] The author integrated the ultrathin inorganic piezoelectric and semiconducting materials onto elastomer substrates, which enabled amplified and low hysteresis measurements of pressure on the skin. The pressure sensing results showed high sensitivity (~ 0.005 Pa) and fast response time (~ 0.1 ms). The devices can be attached to wrist and neck for monitoring artery pulse for a long time, without allergic reactions, redness or damage to the human skin. In addition, Pan's group first demonstrated a new type of transparent and flexible ultrasensitive tactile sensors made by iontronic microdroplet array and microfluidic films.[182-184] The overall device with packaging can be as thin as $200\text{ }\mu\text{m}$ with an optical transparency better than 80%. These devices were utilized as artery pulse monitors to measure the radial arterial pressure waveform, which readily recognized all of the key features of the waveform (P-wave, T-wave, and D-wave).

Besides wrist pulse, the deep-lying internal jugular venous pulse (JVP) is considered another crucial parameter for the detection of conditions such as arrhythmias, right heart hemodynamics, or pericardial disease.[185, 186] Bao's group first demonstrated the monitoring of JVP by microhair-based capacitive pressure sensors.[11] The contact between sensors and the irregular surface of the epidermis was improved by the microhair-structured interfacial layers, and gave rise to the remarkable signal amplification (Figure 2.7a). Recently, Hyunhyub Ko's group reported an interlocked structure based e-skins. They used the device to investigate temperature dependent variation of the pulse pressure from wrist artery, and found that the pulse and reflected wave pressure (P1, P2, and P3)

decreased with an increase of the body temperature (Figure 2.7f-h).[187] The simultaneous monitoring of body temperature and wrist pulse pressure provides a new way of establishing blood pressure by accounting the individual's skin temperature.

2.2.3 Body Temperature

Core body temperature is one of the most important parameters for clinical judgment and health management. Abnormal body temperature indicates a serious threat to a patient's health. For example, when a patient is suffering from trauma and sepsis, core body temperature is considered to be a critical index for monitoring health status. Traditional detection method requires the clinical thermometer and an invasive telemetric device to be inserted into the patient's body (oesophagus, rectum, mouth, or external auditory meatus/tympanic membrane), which causes discomfort and potential infection for the sick person.[188] Such methods for the detection of skin and axillary temperatures correlate poorly with the core temperatures, and rectal temperatures are generally inconvenient and potentially dangerous in neonates. The use of tympanic membrane probes to measure body temperature is shown to be a reliable method, but it still limited at detecting clinical fevers in a pediatric outpatient setting.[189, 190] Flexible temperature sensing devices will overcome the above problems owing to their biocompatibility and mechanical flexibility. Recently, Rogers' group demonstrated epidermal electronics and epidermal heat flux sensors for non-invasive monitoring of core body temperature.[5, 191-195] The ultrathin device can be attached subtly and reversibly onto the skin's surface (**Figure 2.8a-c, e**). The devices can be built by polyurethane (PU) foam to realize the strong bending deformations, where the bending radius can reach up to ~ 10 mm (Figure 2.8d and e). With the modeling algorithm in theoretical approach, these devices can assess core body temperature (Figure 2.8f). The finite element analysis (FEA) results showed that the PU based sensors have similar response time with silicone based sensors (Figure 2.8g).[194] By combining colorimetric temperature indicators (thermochromic liquid crystals) and wireless stretchable electronics, they also reported ultrathin photonic devices and their applications in non-invasive spatial mapping of skin temperature with milli-Kelvin precision (± 50 mK) and sub-millimeter spatial resolution.[193]

Figure 2.8 Flexible sensors on detection of body temperature. a, b) Photograph and infrared image of epidermal electronics attached to human skin; Reproduced with permission.[192] Copyright 2013, Nature Publishing Group; c) Temperature of the palm measured with an infrared camera and a flexible sensor array; d, e) PU foam based bendable temperature sensors; f, g) FEA results for transient effects in the thermal conduction model. Reproduced with permission.[194] Copyright 2015, Wiley-VCH.

The composites of conductive materials and temperature sensitive polymers have been demonstrated to be promising materials for the construction of temperature sensors.[196] For example, the Ni microparticles-filled binary polymers of polyethylene (PE) and polyethylene oxide (PEO) showed higher sensitivity for monitoring human body temperature.[197] By integrating it with a passive radio frequency identification (RFID) antenna, the authors demonstrated the wireless temperature sensor with a sensitivity of 0.3 V/°C, which is ~3 orders larger than standard thermocouple devices. Recently, Takei's group exploited printing technology to fabricate flexible three-axis tactile and temperature sensor arrays. The temperature sensitive material is a composite of CNT and

PEDOT:PSS.[78, 89, 198] The devices showed high temperature sensitivity of $\sim 0.61\%/^{\circ}\text{C}$ in the temperature range between 21°C and 50°C , which is ~ 3 orders larger than that of multiwalled CNTs ($\sim 0.00061\%/^{\circ}\text{C}$), and better than graphene nanowalls-based device ($\sim 0.234\%/^{\circ}\text{C}$) on PDMS substrate and Pt thermal sensor ($\sim 0.53\%/^{\circ}\text{C}$) fabricated on a flexible substrate.[196, 199]

Temperature coefficient of resistance (TCR) value is a key parameter to evaluate the temperature sensing properties of a material. High TCR value provides high sensitivity for resistance type temperature sensors. It should be noted that the TCR value is dynamically changed at different temperature ranges for a certain material. For monitoring body temperature, the wearable device requires the sensing material to have a high TCR in the temperature range of 34°C to 42°C , which is the crucial range for the human body. The resolution of the sensing devices should reach up to $\sim 0.1^{\circ}\text{C}$ for daily healthcare, and $\sim 0.01^{\circ}\text{C}$ for clinical practice.

2.2.4 Other Flexible Health Monitoring Sensors

Ultrathin flexible electronics provide a minimally invasive monitoring system for in vivo diagnostics and therapeutic practices, where conventional devices based on rigid microelectrode arrays bring the possibility of damaging adjacent soft tissue with their intrinsic rigidity.

For monitoring electrophysiological (EP) signals, such as electroencephalograms (EEGs), electrocardiograms (ECGs), and electromyograms (EMGs), Rogers' group demonstrated the use of flexible electrode arrays and epidemic electronics to track the activity of the brain, heart, and muscle tissues (**Figure 2.9a-c**).[5, 191, 200, 201] This ultrathin tattoo-like electronic device consists of multiple components, including transistors, light-emitting diodes, circuit elements, wireless power coils, and radio-frequency communication modules. The authors also demonstrated that the resulting data contained sufficient information for human-machine interactions (Figure 2.9c).[202, 203] Capacitive epidermal electronics for EP measurement allows the electrode materials to be fully encapsulated and

protected from the surroundings. The isolated electronics and electrodes provide advantages in measuring EP signals of internal organs, which could enhance safety by minimizing leakage currents and avoiding irritation/allergic reactions. In vivo studies with animal (rabbit, rat, pig, and cat) models demonstrated the capabilities of these devices at monitoring and spatially mapping temperature, cardiac EP signals, strain, and physical contact.[204, 205] Besides, nanostructured dry electrodes such as micropillars and carbon nanomaterials have been employed for monitoring the EP signals.[206, 207] These results indicate that the ultrathin flexible/attachable electronic device provides a powerful and revolutionary tool for clinical practices and basic neuroscience research.

Real-time tracking of intraocular pressure (IOP) is considered as a promising way to pre-diagnose glaucoma disease.[208, 209] It is extremely challenging to build the exact relationships between the kinetics, duration and magnitude of IOP elevation and optic nerve damage in human eye, because IOP dynamically changes each day and measuring the values over a long-term is difficult.[210, 211] The high-sensitive, transparent, and flexible pressure sensors show great potential for remote IOP monitoring systems. The microfluidic pressure sensors and various Si-based sensors have been developed to measure IOP, but they affect the eyes over long periods of measurements (Figure 2.9d).[209, 212] With MEMS technology, Ha et al. reported a polymer-based capacitive flexible pressure sensor for monitoring IOP in a mouse's eye.[213] This device featured small size ($30 \times 300 \times 300 \mu\text{m}^3$) and high sensitivity (0.3 Ff/mmHg), which provided the needed resolution for IOP monitoring. Recently, Troster's group demonstrated ultrathin transistors equipped smart contact lenses that could serve to measure IOP (Figure 2.9e).[214] They proposed a wafer-scale process scheme to realize flexible, lightweight and transparent electronics on top of a $1 \mu\text{m}$ thick parylene film that was released from the carrier substrate after the dissolution in water of a polyvinyl-alcohol layer. The thin and flexible devices can be transferred to plastic contact lenses, equipped onto an artificial eye, and still be highly sensitive to small strains like transistors (Figure 2.9f and g). Sensimed, a Switzerland company, has commercialized the smart contact lenses with embedded microsensors to continuously monitor IOP.

Figure 2.9 The application of flexible sensing devices on monitoring electrophysiological signals and IOP. a) Photograph of attachable epidermal electronics on human skin; b) ECG and EMG signals measured with the flexible sensing device attached to the chest and leg respectively; Reproduced with permission.[5] Copyright 2011, AAAS; c) Surface electromyography (sEMG) signals recorded from both forearms with four types of gestures; Reproduced with permission.[202] Copyright 2013, Wiley-VCH; d) The IOP measurement system embedded in an intraocular lens; Reproduced with permission.[209] Copyright 2014, Nature Publishing Group; e, f) The transparent TFTs base sensor on a plastic contact lens and an artificial eye; g) Device response to applied strain. Reproduced with permission.[214] Copyright 2014, Nature Publishing Group.

Besides the above examples, flexible pressure sensors possess the capability to continuously assess the foot plantar pressure, which is crucial in the treatment and prevention of plantar ulcerations for diabetes patients.[2, 3] In addition, Bansal et al. reported flexible organic optoelectronic sensors by the combination of organic light-

emitting diodes (OLEDs) and organic photodiodes (OPDs), and demonstrated their applications in monitoring the signals from intact muscle and tissue oxygenation.[215] Based on near-infrared spectroscopy (NIRS) technology, the devices can measure the blood oxygenation by detecting the changes of optical properties of endogenous chromophores such as oxygenated (HbO_2) and deoxygenated hemoglobin (Hb). These wearable and light-weight organic electronics show great potential in the next generation of low-cost, disposable, and non-invasive optical sensors for medicine and sports. In addition, the flexible strain sensor and pressure sensor can be used to monitor health related mechanical signals such as physical motion, joint recovery, and Parkinson's tremors.[22, 23, 28]

2.3 Questions to Answer Based on Literature

Many challenges still lie ahead before implementation of such flexible sensing devices in practical applications. For example, it is sometimes difficult to distinguish the physiological signals from noisy background signals. High performance pressure and strain sensors are sensitive to the human motion and movement, and will produce large noisy signals when placed on the human body. To be successful in the commercialization of wearable devices, cost-effective packaging and manufacturing methods, with large-scale and mass customizations, should be demonstrated during fabrication of the flexible sensors. For manufacturing technology, the traditional method cannot produce sensing devices with high accuracy and minimization. The new micro-manufacturing technologies, such as flexible MEMS and 3D printing electronic technology, could reduce the fabricating costs and enable the large-scale and mass production of flexible electronic sensing devices. The large-scale fabrication can be achieved by printing multiple devices simultaneously, rather than the traditional step-by-step and one-by-one manufacturing technology. For the new products and designs, the printing technology requires change of designs to be made in computer, without the facility changing in the production line. Therefore, low-cost manufacture such as printing technology will eradicate the cost barrier for commercialization of such flexible health monitoring devices. Also, solutions are needed to decrease the power consumption of devices, which will prolong the working duration by

minimizing the battery consumption. Self-power sensing devices have been developed to meet the power demands of wearable health monitoring system.[216-219] There still needs to develop the replaceable and flexible power source with continuable and long-time output. Beyond passive tracking and monitoring, wearable electronic devices could be integrated with micro-actuators for interaction with the human body and pave the way for the new concept of wearable/attachable healthcare devices.

2.4 PhD in Context of Literature

For resolving all the above problems, the novel and advanced materials, the new device configurations, as well as new manufacturing technology are required for flexible sensing electronics. The novel and advanced materials such as programmable and flexible conductors or semiconductors will open the new opportunity for the flexible electronic device. For example, the programmable high crystallinity carbon patterns, introduced in *Chapter 4*, shows higher performance in detection of bending and vibrations, and promising for integrated and modularized sensor arrays. Self-crosslinked carbon arrays in *Chapter 5*, presents high sensitivity and good stability (~10,000 times) in the detection of flexions due to their special structures such as self-crosslinked points and vertically aligned nanorods. The ultrathin CdS film in *Chapter 6*, were demonstrated with unprecedented vertical piezoelectricity d_{33} , and be used for construction of piezoelectric pressure and strain sensors, which will show ultrahigh sensitivity and fast response time and make the device with new functionality. Minimization of flexible sensing electronics put device towards smaller, smart, and less power consumption. In *chapter 7*, the micro-manufacturing technologies can minimize the flexible sensors by integration. All materials and technologies developed in this thesis pave the way for flexible sensing electronics and flexible health monitoring system.

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Chapter 3

Experimental Methodology

This chapter presents the overall experimental methods for the thesis work. The principles for selection of materials and synthesis of materials are described in Section 3.1. The techniques and theories used for material characterization including scanning electron microscopy (SEM), optical microscopy (OM), transmission electron microscopy (TEM), Raman, atom force microscopy (AFM), dual ac resonance tracking piezoelectric force microscopy (DART-PFM) are discussed in Section 3.2. The simulation and calculation for experiment results are elaborated in Section 3.3. Finally, the micro-manufacturing methods for device fabrication are introduced.

3.1 Rationales for Synthesis of Materials

3.1.1 Selection of Materials

In this PhD project, the carbon nanomaterials with novel structures were proposed for construction of flexible sensing electronics as active materials or electrode materials. Their good conductivity and mechanical properties provide a valuable opportunity in fabrication of piezo-resistance type mechanical sensors such as pressure sensors, strain sensors, and vibration sensors. However, the hysteresis of piezo-resistance flexible sensors makes the device shows slow response time, and cast shadow on their applications. To resolve this problem, the piezo-electric materials like CdS with ultrathin configuration were designed for high-sensitive piezoelectric flexible sensors. The piezo-effect is instantaneously occurred when apply the pressure and strain to the non-centrosymmetric crystals. Therefore, the piezoelectric flexible sensor possesses very fast response time in detection of mechanical stimulations, which is beneficial for monitoring the health-related body vibrations.

3.1.2 Chemical Vapor Deposition

There are many method for synthesis of nanomaterials, such as wet chemistry method and vapor phase method. Among them, the chemical vapor deposition (CVD) method is to be considered an effective way to synthesize nanomaterials for electronic applications which require high crystallinity and controllable lattice defects [1-3]. Typically, the precursors were brought into the tube furnace by carrier gas, and reacted with substrate (or other chemicals) at high temperature to form target materials. For example, as the conventional CVD method for growth of graphene (**Figure 3.1**), the carbon precursor such as CH_4 was introduced into a furnace to react with metal catalyst (Ni, Cu, etc.) at high temperature, then absorbed to metal catalyst and reaches to saturated Ni/C alloy. The graphene can be synthesized in the cooling down process. By changing the parameters such as pressure and catalyst geometry, various carbon nanostructures (including amorphous carbon film, SWCNT, MWCNT, graphene, high crystallinity carbon patterns, and self-crosslinked

carbon arrays, etc.) can be readily achieved. The detailed process for synthesis of high crystallinity carbon, self-crosslinked carbon array, and CdS ultrathin film are described at the followed chapters of experimental method section.

Figure 3.1 Experimental setup of the typical CVD process for growth of graphene.

3.2 Characterization

The scanning electron microscopy (SEM), optical microscopy (OM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are important tools to explore the micro/nano-structures of prepared nanomaterials.

3.2.1 Scanning Electron Microscopy (SEM)

The main components of a typical SEM instrument are electronic console, electron column, scanning system, signal detectors, and vacuum system (**Figure 3.2**). The electronic console

provides control knobs and switches which can be used to adjust the instrument by filament current, accelerating voltage, focus, magnification, brightness and contrast.

Figure 3.2 Layout of components in a basic SEM [5].

The electron column of the SEM consists of an electron gun and two or more electromagnetic lenses operating in vacuum. The electron beam was generated under vacuum. The electron lenses were used to focus the electron beam on the surface of a specimen with small diameter. When the electron beam scanned to surface of a specimen, their interactions will generate several of signals which showing the characteristics at and near the surface of a specimen (**Figure 3.3**). For example, the secondary electrons generated from the inelastic collision and scattering of incident electrons with specimen electrons. They are generally characterized by possessing energies of less than 50 eV [4-5], and can be used to reveal the surface structure of a material with a resolution down to nanoscale. Backscattered electrons are a result of an elastic collision and scattering event

between incident electrons and specimen nuclei or electrons. Backscattered electrons can be generated further from the surface of the material and help to resolve topographical contrast and atomic number contrast with a resolution of >1 micron. Besides, the X-ray signal is the common signal that used in SEM for determination of the materials' composition by energy dispersive X-ray spectroscopy (EDS) analysis. The signal detectors such as the secondary electron detector and backscattered electron detector were located around the sample stage inside the chamber. The signals can be collected by detectors to display the morphology and element dispersion of sample surface. The SEM can reach the resolution down to nanoscale (the resolution from the field emitter is higher than that from thermionic emitter), and therefore be used to characterize the sample morphology and composite in this PhD project.

Figure 3.3 Schematic illustration of interaction between the electrons and specimen.

3.2.2 Transmission Electron Microscopy (TEM)

TEM is by far one of the most important tools for studying microstructure of materials, where a high-energy beam of electrons is transmitted through an ultra-thin specimen, and interacted with the specimen when passes through it. The generated signals from the interactions between the electrons and specimens can be collected to observe the features in the structure like crystal structure, dislocations, grain boundaries, and detects in detail.

Typically, a TEM is composed of several components (**Figure 3.4**), including a vacuum system, an electron gun for generation of the electron beam, a series of electromagnetic lenses (condenser lens, objective lens, diffraction lens, projector lens), as well as a series apertures. These components can be used to guide and manipulate the electron beam. The electron beam will be interacted with the materials to produce the signals for imaging. Imaging devices such as charge-coupled device (CCD) camera are subsequently used to create an image from the electrons that exit the system. This PhD project employed the TEM to study the microstructures of materials, for example, the TEM was used to investigate the defects and cross section structures of self-crosslinked carbon arrays.

Figure 3.4 Layout of components in a basic TEM [5].

3.2.3 Optical Microscopy (OM) for Atomic Thin Materials

The optical microscopy focused the light by a set of optic lenses and produced 5 to 1000 magnifying power. Traditionally, the OM only can realize the resolution to $\sim 1 \mu\text{m}$ due to the wavelength limitation of visible light source (from ~ 380 to ~ 780 nm). It is interesting that the OM is strongly capable in observation of atomic thin materials on SiO_2/Si substrate, especially the thickness of the materials can be down to sub-nano scale [6-10]. The materials with various thickness on SiO_2/Si substrate will present different contrast values, which were recorded by Charge-coupled Device (CCD), and can be easily measured by Red (R), Green (G), and Blue (B) values at each pixel of optical images. The contrast (C) can be calculated by the Fresnel equation under normal incident conditions as follows [7]:

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)}$$

$$C_D(\lambda) = C(\lambda) - C_S(\lambda)$$

Where λ is the wavelength of the incident electromagnetic wave, R and R_0 are the reflected light intensity by the multilayer structure with and without materials. C_D is the contrast difference, and C_S is the contrast value on substrate.

As an example [8], **Figure 3.5a** shows the optical microscopy image of an ultrathin MoS_2 flake on 90 nm SiO_2/Si . Figure 3.5b is the contrast profile of the dashed rectangle highlighted in Figure 1a generated. The contrast values of the octuple-layer (8L) and hexuple-layer (6L) MoS_2 nanosheets are 162.3 and 118.6, respectively, while the contrast value of 90 nm SiO_2/Si is 120.4. The contrast difference between the MoS_2 nanosheet and SiO_2/Si substrate is 41.9 for 8L MoS_2 , and -1.8 for 6L MoS_2 . The contrasts have a linear relationship with the sample thickness. Therefore, the OM can be employed to rapidly identify the thickness of our 2D materials like CdS ultrathin film and graphene. The accurate thickness will be further measured by the AFM equipment.

Figure 3.5 (a) Optical microscopy image of 2D materials on SiO_2/Si substrate; (b) Contrast profile of the dashed rectangle shown in a [8]; (c) contrast value with the various thicknesses of InSe samples [9].

3.2.4 Raman Spectrum

The Raman spectroscopy is the technology based on Raman scattering, where the laser photons can be interacted with atomic and molecular of a specimen by molecular vibrations, rotational, and electronic transitions. After the interaction between photons and specimen, the energy of the laser photons will be shifted up and down, which will give information about the vibrational modes of samples for identifying elements, structures, and compounds in the samples. Typically, the Raman spectrum is plotted in terms of the energy shift with respect to the exciting line rather than by absolute wavelength, since it is the energy of this shift which is significant. By integration with the accurate moveable stage, the Raman shift can be collected from a very small area step by step for Raman mapping. This Raman shift mapping provides a very high spatial resolution, and can be used to study the distribution of materials in microscale or nanoscale. This PhD project employed the Raman spectroscopy to investigate the structures and component of prepared samples, for example, the Raman shift was used to identify various carbon materials by different vibration modes of carbon atoms.

3.2.5 Atomic Force Microscopy (AFM)

The AFM can be used for in-situ characterization for the surface information of sample such as topography, conductivity, surface charge dispersion, and electromechanical properties. For measurement of topography, there are tapping mode and contact mode between the AFM tip and samples. The tapping mode is a most effective way to get the topography of sample surface and avoid destroying the sample. At this situation, the cantilever is typically oscillated mechanically by a small piezo electric actuator which was located closed to cantilever. At first step, the resonance of cantilever should be detected by driven frequency scanned over a wide range. Then, the driven frequency should be set at (or close to) the resonance frequency of cantilever. The laser driven optical detector was used to measure the oscillatory motion of the cantilever, and the electronic device inside the controller measures the amplitude of this oscillation. Typically, the repulsive tapping mode is the common mode in conducting the AFM scanning, where the AFM tip is in repulsive contact with the sample surface in some fraction of its oscillation. The contact mode can be used to apply the pressure and external potential to the sample surface. The detailed working theory described in following parts (3.2.6).

3.2.6 DART-PFM

As shown in **Figure 3.6**, the AFM cantilever is driven by two different frequencies, f_1 and f_2 , which are close the resonance of eigenmodes [10]. The resulting cantilever deflection is used as the input for two separate lock-in amplifiers, where f_1 is used as a reference for one lock-in, and f_2 is as a reference for another one. The corresponding amplitudes from two driven frequencies (f_1 and f_2) are A_1 and A_2 respectively. When the interaction of tip and sample was changed, the response curve of resonant frequency will shift toward low frequency (or high frequency). For example, as the frequency shifts toward low frequency (from solid curve to dashed curve in inset of Figure 3.6), the amplitude A_1 will moves up to A_1' , while A_2 move down to A_2' . The signal amplitude difference ($A_2 - A_1$) can be used as an input to feedback loop, and to respond by shifting the drive frequencies until the signal amplitude difference is zero, where the differential ($\Delta f = f_2 - f_1$) of drive frequencies is

constant. For a symmetric peak, the resonant frequency can be calculated by the formula of $f_c = (f_2 + f_1)/2$. Therefore, tracking the change of resonant frequency provides an effective way to depict electromechanical behavior at the sample's surface, such as contact stiffness of the tip-surface contact during scanning. In the process of PFM and DART-PFM scanning, the frequency and the main tip force applied to the sample are slightly changed when using different tips. For DART-PFM scanning process, AFM cantilever is driven by two different frequencies (f_1 and f_2) with the differential ($\Delta f = f_2 - f_1$) of 10 kHz.

Figure 3.6 Schematic illustration of experimental set-up for DART-PFM. Inset shows the principle of the dual-frequency excitation by resonant-amplitude tracking.

3.3 Simulation and Calculation

3.3.1 FE Simulation by COMSOL Multiphysics

The FE simulation of the vertical piezoelectricity and sub-atom deformation actuator were conducted using a finite element modelling software (COMSOL Multiphysics 5.0). The PFM tip was modeled as a hemisphere with the diameter of ~50 nm, which is corresponding

to the radius (~25 nm) of used PFM tip (as determined by SEM, Fig. 6B). The CdS sample was modeled with the thickness of 3 nm.

The elastic matrix c has 5 independent parameters, and piezoelectric coefficient d has three independent parameters.

Elastic matrix c :

$$c_{11}=c_{12}=c_{21}=8.665 \times 10^{10} \text{ Pa}$$

$$c_{13}=c_{31}=c_{23}=c_{32}=4.614 \times 10^{10} \text{ Pa}$$

$$c_{33}=9.361 \times 10^{10} \text{ Pa}$$

$$c_{44}=1.486 \times 10^{10} \text{ Pa}$$

$$c_{55}=1.622 \times 10^{10} \text{ Pa}$$

Piezoelectric coefficient d :

$$d_{31}=d_{32}= -5.09 \times 10^{-12} \text{ C/N}$$

$$d_{33}= 32.8 \times 10^{-12} \text{ C/N}$$

$$d_{15}= -11.91 \times 10^{-12} \text{ C/N}$$

Then, the piezoelectric coupling matrix is:

$$e = cd^T$$

$$\begin{aligned}
 &= \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(c_{11} - c_{12}) \end{bmatrix} \times \begin{bmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{31} \\ 0 & 0 & d_{33} \\ 0 & d_{15} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \\
 &= \begin{bmatrix} 8.665 & 0 & 4.614 & 0 & 0 & 0 \\ 0 & 8.665 & 4.614 & 0 & 0 & 0 \\ 4.614 & 4.614 & 9.361 & 3 & 0 & 0 \\ 0 & 0 & 0 & 1.486 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1.622 & 0 \\ 0 & 0 & 0 & 0 & 0 & 17.2 \end{bmatrix} \times 10^{10} \text{ Pa} \times \begin{bmatrix} 0 & 0 & -5.09 \\ 0 & 0 & -5.09 \\ 0 & 0 & 32.8 \\ 0 & -11.91 & 0 \\ -11.91 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ C/N} \\
 &= \begin{bmatrix} 0 & 0 & 1.073 \\ 0 & 0 & 1.073 \\ 0 & 0 & 2.6051 \\ 0 & -0.177 & 0 \\ -0.177 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ C/m}^2
 \end{aligned}$$

Elasticity matrix

$$\begin{bmatrix} 8.665 & 0 & 4.614 & 0 & 0 & 0 \\ 0 & 8.665 & 4.614 & 0 & 0 & 0 \\ 4.614 & 4.614 & 9.361 & 3 & 0 & 0 \\ 0 & 0 & 0 & 1.486 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1.622 & 0 \\ 0 & 0 & 0 & 0 & 0 & 17.2 \end{bmatrix} \times 10^{10} \text{ Pa}$$

Density: 4826 Kg/m³

Relative permittivity: 8.73

Complete mesh consists of 979 domain elements, 548 boundary elements, and 68 edge elements.

Number of degrees of freedom solved for: 7560.

3.3.2 Calculation of Conductivity, Carrier Concentration and Mobility

Conductivity (σ) is the inverse of the resistivity (ρ), which can be calculated by resistance (R) for 3D material system (bulk materials) and sheet resistance (R_s) for 2D materials system (thin film). The unit of conductivity is S/m (1 S/cm = 100 S/m).

For 3D material system, the conductivity σ is defined as:

$$\sigma = \rho^{-1} = \frac{l}{RA}$$

where l is the length of material,

R is the resistance,

and A is the cross-section area.

For 2D materials system, the conductivity σ can be calculated by the following equation:

$$\sigma = \rho^{-1} = \frac{1}{R_s w}$$

where w is the thickness of material.

Carrier Concentration (n) is the concentration both of electrons and holes in materials, which can be derived from the follow equations:

$$J = I/A = \frac{nqV_d A}{A} = nqV_d$$

Where J is the current density.

n is the carrier concentration

q is the electrical charge

V_d is the drift velocity

A is the cross-section area of charge flow.

The **mobility** (μ) is defined as:

$$\mu = V_d/E$$

where E is the applied field.

Therefore, the conductivity can be express by the mobility and carrier concentration:

$$\sigma = \frac{J}{E} = \frac{I}{AE} = \frac{nqV_d}{E} = nq\mu$$

$$n = \frac{\sigma}{q\mu} = \frac{1}{\rho q\mu}$$

Mobility (μ) is a measure of how easily the charge carriers move under the influence of an applied field or how mobile the charge carriers are. Typically, it can be obtained by the performance of FET device via following equation:

$$\mu = G_m \frac{L}{WC_g V_{ds}}$$

Where G_m is the peak transconductance, which can be calculated by

$$G = \frac{dI_{ds}}{dV_g}$$

C_g is the gate capacitance (1.1×10^{-8} for 290 nm SiO₂ on Si substrate).

L and W are the channel length and width respectively.

3.4 Device fabrication

3.4.1 Photolithography

Photolithography was considers the effective way for micro-manufacturing process. The photoresist is sensitive to UV light and can be modified after UV light exposure. The various micro-patterns of photoresist can be obtained by limit the UV light by shadow mask

with desired micro-patterns. As shown in **Figure 3.7**, the typical process including the following steps: i) cleaning the substrate by acetone, ethanol, IPA, etc; ii) spin coating photoresist to substrate; iii) pre-bake for solidification of photoresist; iv) mask aligner exposure; v) developing to get micro-patterned photoresist; v) metal film depositing by e-beam deposition. The metal electrode such as Au/Ti, Au/Cr, Cu/Ti, and Cu/Cr can be prepared after lift-off at acetone solution, which will resolve the undesired photoresist at substrate. The detailed fabrication for micro-patterned photoresist, carbon-based Hall devices, and CdS FETs have been described at following chapters.

Figure 3.7 Schematic for photolithography process.

3.4.2 Wet Etching and Dry Etching

For patterning the substrate by MEMS technology, the wet etching and dry etching were employed for etching the Si, SiO₂, PDMS, PI substrate. Various geometry can be achieved by photolithography with positive (or negative) photoresist. The photoresist can be used to protect the substrate where not required be etching. The photoresist such as AZ 5214E can be used in wet etching of SiO₂ by buffered oxide etch (BOE) solution, and dry etching of SiO₂ by PECVD in a certain situation. However, the photoresist cannot plays as protect template for wet etching of Si because it will be resolved in etching solution such as NaOH. To resolve this problem, SiO₂ and the metal film such as Au and Ni can be deposited, as

protect template for wet etching. The metal film can be removed by acid solution and gold etch (TYPE-TFA) solution. For patterning the polymer substrates such as PDMS and PI, this thesis employed the dry etching of PECVD with CF_4 and O_2 gases. The etching parameters for different materials are listed as followed Table 3.1.

Table 3.1 Typical etching experiments in this thesis.

Materials	Method	Solution/ Atmosphere	Reaction time (min)	Temperature	Template
SiO_2	Wet etching	BOE	2-3 min for 290 nm	RT	PRAZ5214 (positive and negative)
SiO_2	Dry etching (PECVD)	CF_4 , O_2	5-6 min for 290 nm	25°	PRAZ5214 (positive only)
Si	Wet etching	35% NaOH	45 min	85° (Oil bath)	290 nm SiO_2
PDMS	Dry etching (PECVD)	CF_4 , : O_2 60:20 sccm	4 h for 50 μm	25°	Metal (Cu)
PI	Dry etching (PECVD)	CF_4 , : O_2 20:60 sccm	4 h for 50 μm	25°	Metal (Cu)
C	Dry etching (PECVD)	O_2 plasma	15 min for 1 μm	25°	

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Chapter 4*

Programmable High Crystallinity Carbon Patterns

Carbon nanomaterials such as carbon nanotube and graphene are promising candidates for next-generation flexible electronics. However, the practical application of carbon electronics requires controlled fabrication of those materials with micro-patterned structures on flexible substrate at wafer-scale and low cost. Inspired by the conventional photolithography process and pyrolysis of photoresist, in this chapter, the new method for synthesis of high-quality micro-patterned high crystallinity carbon was developed. The method employed pre-patterned pyrolyzed photoresist as carbon precursors, to minimize the mobility of carbon during the high temperature growth, which results into high quality carbon patterns with a lateral resolution up to $\sim 2\ \mu\text{m}$. The flexible carbon electronics are demonstrated by transferring the as-patterned high crystallinity carbon patterns to the flexible substrate, and showing asymmetric tensile-compressive response with high output resolution. These results will pave the way to the next-generation carbon-based flexible electronics and mechanical sensors.

*This section has been published substantially as: “**Xuewen Wang**, Hong Wang, Yang Gu, Wei Fu, Guowei Liu, Yongmin He, Yi Long, Wu Zhao, Ting Zhang, Zheng Liu, Programmable High Crystallinity Carbon Patterns, *2D Materials*, **2017**, 4, 025011.”

4.1 Introduction

Carbon nanomaterials with sp^2 hybridized orbitals, such as graphene and carbon nanotubes, are considered to be great candidates for the next generation of flexible/stretchable electronics. The exceptional electrical and mechanical characteristic of graphene, such as high carrier mobility ($\sim 200,000 \text{ cm}^2/\text{Vs}$) and extreme flexibility, endow it with the great potential to enable unique advances in wide-ranging of applications [1-5]. For example, the graphene films are suitable as transparent electrodes in application of flexible touch panel and photovoltaics due to high conductivity ($\sim 100 \text{ }\Omega/\text{square}$) and transparency ($\sim >90\%$) [6-10]. The graphene-based flexible lithium-ion battery and electrochemical capacitor possess ultrahigh energy density and stable performance under mechanical stress [11-13]. Nevertheless, the practical application of graphene in flexible electronics is still limited due to some bottlenecks have yet to be resolved. For example, the controllable micro-patterning of graphene on flexible substrate at wafer-scale, process compatibility with microelectronic manufacturing procedure and low cost. Such fabrication process should be also compatible with the conventional microelectronic manufacturing procedure such as photolithography and printing electronic technology. High crystallinity carbon pattern may provide another avenue for carbon electronics toward practical applications.

In recent years, many efforts have been devoted on patterning graphene and carbon nanotubes with microstructures and exploring its applications in flexible electronics [1,14-19]. The main strategies have been developed are: (i) guided growth on pre-patterned metal catalyst (Ni or Cu) [14,15]; (ii) laser-induced graphene patterns [16-18]; (iii) post-patterning graphene film by reactive-ion etching (RIE) process [19-22]; and (iv) printing electronic technology by graphene-based inks [23-26]. However, these methods have their disadvantages which largely limit their development toward practical applications. Micro-patterning the robust high crystallinity carbon film is still challenging. The method (i) could provide the graphene patterns with monolayer or few-layers, but it is hardly being transferred without the structural damage in small scale due to its flexibility. The laser-induced technology (ii) produced the patterned graphene with low lateral resolution and limited crystallinity due to the inhomogeneity of laser beam. The method (iii) was limited

used in flexible substrate. Also, the process applied photoresist to graphene for RIE process where the residual organic molecules cast shadows on graphene electrical properties. The highly-dispersed graphene inks were required in printing electronic technology (method iv). Typically, many defects could be induced by hydrophilic groups sitting on graphene and amphiphilic organic surfactant that were used to improve the dispersity and stability of graphene inks [27]. As a result, the lifetime and performance of graphene ink based electronic devices need to be further improved. The lateral resolution of less than 10 μm scale still challenging for printing electronic technology [26,28]. In addition, pyrolysis of photoresist film (PPF) provides an effective and controllable way for carbon patterns, but the products are amorphous carbon with weak crystallinity which will cast shadow on the mechanical and electrical properties [29-38]. Therefore, new technology is urgently required for the controlled synthesis of high crystallinity carbon patterns.

Combining the PPF and conventional photolithography process, herein, an effective method for the synthesis of high-quality micro-patterned carbon was reported, where the pre-patterning pyrolyzed photoresist as the solid carbon precursors. This precursor can produce high crystallinity carbon patterns with a high lateral resolution of $\sim 2\ \mu\text{m}$, which approaches the limit resolution of the traditional near-UV photolithography at hard contact mode and meets the requirement of the most flexible electronics. Bendable electronic devices have been fabricated based on the high-quality micro-patterned carbon. The bendable graphene device can stand the bending angle from 0° to 180° and present distinct output response for tensile and compressive strain with high sensitivity, which makes it promising in the construction of flexible mechanical sensors.

4.2 Experimental Methods

4.2.1 Synthesis

As illustrated in **Figure 4.1**, to precisely synthesize the high crystallinity carbon electrodes with micro-patterned structures, the conventional photolithography process was employed to fabricate micro-patterned carbon precursors by pyrolysis of photoresist (step 1 and step

2). The photoresist films (AZ5214 with the viscosity of ~ 24.0 cSt at ~ 25 °C) on SiO_2/Si substrates were fabricated by a spin coating process, where the thickness in the range of $1.45\text{ }\mu\text{m}$ to $3.24\text{ }\mu\text{m}$ can be achieved by adjusting the spin rate from 6000 to 1000 rpm. The microstructured photoresist patterns can be prepared by the conventional photolithography process. The solid carbon precursors were obtained by pyrolysis of as-prepared photoresist films in flowing H_2/Ar gas atmosphere at 1000 °C for 2 h. The thickness of the carbon precursor is the key to achieve high-resolution for high crystallinity carbon electrode. A small amount of precursor cannot provide sufficient carbon source for the growth of high crystallinity carbon electrodes. With a large amount of precursor, carbon will diffuse everywhere and makes a low resolution of the carbon patterns. The amount of precursor can be controlled by spin-coating rate. Then, the 150 nm Ni film was deposited onto the surface of solid carbon precursor, which is the catalyst for the growth of high crystallinity carbon (step 3). This process was conducted at e-beam deposition system with the voltage of $\sim 4.99\text{ kV}$ and the current of $\sim 90\text{ mA}$. The deposition rate should be slowly (less than 0.10 nm/s) to avoid island-shape grain in the subsequent thermal process. The as-prepared Ni/Carbon film on SiO_2/Si substrate was placed at the center of the quartz tube and connected to H_2/Ar gas (H_2 : 5 sccm , Ar : 95 sccm). After mechanical pumping to $\sim 2.2\text{ mBar}$, the tube furnace was heated to 900 °C for 20 min and kept for 1h at 900 °C. Then, the quartz tube was suddenly cooling down to room temperature within 5min, by opening the furnace (NOT the quartz tube) and keeping draught with an electric fan (step 4). After that, the carbon atoms will be segregated from the Ni catalyst film and form high crystallinity carbon at the surface, and exactly followed the geometries of the carbon precursor patterns under the Ni film.

4.2.2 Transferring of Materials onto the Flexible Substrate

To investigate their properties and broaden the applications, as-prepared high crystallinity carbon patterns have been transferred to the flexible substrates, such as PDMS and PET (step 5 in Figure 4.1). The PMMA was spin-coated to the sample surface at 2000 rpm and baked at 120 °C for 4 min to evaporate the solvent for solidification.

Figure 4.1 Schematic illustration of the manufacturing process for the synthesis of micro-patterned high crystallinity carbon electrodes.

The PMMA/carbon film can be peeled off from the SiO_2/Si substrate by etching the Ni catalyst in 1M FeCl_3 solution at for ~5 h, after washing several times with deionized water, and then transferred and attached it to a target PET and PDMS substrate. Finally, the high crystallinity carbon pattern was transferred to target substrate after removing the PMMA film by acetone. For transferring of high crystallinity carbon pattern to elastic PDMS film, the PDMS mixture (Dow Corning Sylgard 184; the weight ratio of base to cross-linker was 10:1, the details can be found elsewhere [39]) was spin-coated to carbon/ SiO_2/Si substrate at ~600 rpm, and solidified at 85 °C for 2 h to form the solid elastic film on the substrate. Then, the elastic PDMS film with high crystallinity carbon sample was immersed into 1M FeCl_3 solution for ~10 h, and rinsed in DI water for several times, and can be peeled off from the SiO_2/Si substrate to get carbon/PDMS film.

4.2.3 Characterization and Performance Evaluation

The quality and microstructures of synthesized high crystallinity carbon was characterized by optical microscopy (Olympus BX51), SEM (JEOL-6700F), AFM (Cypher S, Asylum

Research), and Raman (WITec alpha300 RAS Raman system). The multi-channel potentiostat (Bio-logic VMP3) and LabVIEW controlled digital source meter (Keithley 2450) were used to measure the resistance change in real-time, and the Source-Drain voltage was 2 VDC. The home-made translation stage with the step of $\sim 20\ \mu\text{m}$ was used to load the bending to device.

4.3 Results and Discussion

Figure 4.2a and **b** show the optical images of patterned high crystallinity carbon on Ni/C/SiO₂/Si substrate and transferred carbon electrode on PDMS substrate. The results indicate that the patterned high crystallinity carbon electrodes on the original substrate are totally transferred to flexible PDMS substrate, and the microstructures are not destroyed in the transferring process. To investigate the quality of as-prepared high crystallinity carbon electrodes, the Raman spectra was collected from the as-grown high crystallinity carbon patterns at different locations. The typical Raman spectra of patterned high crystallinity carbon and carbon precursor are shown in **Figure 4.2c** (red for high crystallinity carbon and blue for carbon precursor). The weak disorder induced D band at $\sim 1355\ \text{cm}^{-1}$ and strong 2D band at $\sim 2700\ \text{cm}^{-1}$ suggest the high-quality of the high crystallinity carbon. The strong G-band around $1586\ \text{cm}^{-1}$ indicates excellent crystallinity. The full width at half-maximum (FWHM) of the 2D band is around $30\ \text{cm}^{-1}$, and the intensity ratio of 2D band to G band (I_{2D}/I_G) is about 0.5, both of which are the characteristic Raman peaks of the high crystallinity carbon. To evaluate thickness and quality homogeneity ($> 100\ \mu\text{m}$), the Raman mapping has been performed from the marked square i in **Figure 4.2a**. **Figure 4.2d-f** show the Raman intensity mapping at G and 2D peak, and the mapping of 2D /G (intensity), respectively. The Raman mappings clearly indicate the high crystallinity carbon patterns are contiguous film with consistent high quality over large area. They are also supported by the peak position mapping (**Figure 4.3**).

Figure 4.2 Micro-patterned high crystallinity carbon electrodes. The photographs of high crystallinity carbon electrodes on Ni/SiO₂/Si substrate (a) and flexible PDMS substrate (b), the scale bar is 500 μm . (c) The Raman spectrum collected from the carbon precursor (blue curve) and synthesized high crystallinity carbon (red curve). The G-band (d) and 2D-band (e) Raman mapping collected from point i in a (marked by blue square), indicating the uniform and high-quality carbon was synthesized. The statistic histogram (g) and mapping (f) for the intensity ratio of 2D/G. (h) Optical microscopy image of high crystallinity carbon electrodes on Ni/SiO₂/Si substrate, the scale bar is 20 μm . The G-band (i) and 2D-band (j) Raman mapping collected from micro-patterned high crystallinity carbon electrodes. (k) The statistic histogram of FWHM from 2D-band.

Figure 4.3 (a) the typical Raman spectrum of prepared high crystallinity carbon film. (b and b-1) Raman shift position mapping at $\sim 1355 \text{ cm}^{-1}$ for D-band. (c and c-1) Raman shift position mapping at $\sim 1586 \text{ cm}^{-1}$ for G-band. (d and d-1) Raman shift position mapping at $\sim 2700 \text{ cm}^{-1}$ for 2D-band.

Figure 4.2h shows the statistic histogram of I_{2D}/I_G by counting 10000 points at $140 \times 140 \mu\text{m}^2$ region (from Figure 4.2f). The values of I_{2D}/I_G distributed in the range of 0.4 to 0.9 with near-Gaussian distribution, which suggesting that the as-synthesized high crystallinity carbon is multiple layers. The coverage of multiple layer high crystallinity carbon on Ni/C is $\sim 100\%$. SEM characterization further demonstrates the uniformity of multiple layers high crystallinity carbon and their thickness is around $\sim 100 \text{ nm}$ from surface profiler

(**Figure 4.4**). Figure 4.2h shows the optical microscopic image from marked square ii in Figure 4.2a, and the corresponding Raman mappings are displayed in Figure 4.2i and j, respectively. Notably, the high crystallinity carbon electrodes with channel gap around 20 μm were fabricated. The high crystallinity carbon electrode size is similar to the original carbon precursor (**Figure 4.5**). The G peak and 2D peak position mappings indicate that the high crystallinity carbon was grown exactly following the geometries of the carbon precursors and no epitaxial growth is found along the substrate surface (outside of carbon precursors). The microscopy images and Raman mapping images of transferred high crystallinity carbon patterns on PDMS substrate indicate the target carbon materials with various patterns were successfully transferred to PDMS substrate (**Figure 4.6**). The SEM images (**Figure 4.7a-c**) indicate porous structures and few layer graphene existed in the synthesized high crystallinity carbon patterns. Typically, the epitaxial growth of graphene makes the pre-fabricated micro-patterns fuzzy and indistinct, and therefore decrease the resolution of the electrode. With optimized parameters, the method can realize the local growth of high crystallinity carbon electrode with high resolution, and the line width and channel gap can be less than 2 μm (**Figure 4.7d-h**), which is close to the limit resolution of the traditional near-UV photolithography at hard contact mode and soft contact mode.

Figure 4.4 Height profile of high crystallinity carbon measured by the surface profiler.

Figure 4.5 Optical microscopic images of pre-patterned photoresist (a), pyrolyzed carbon precursor (b), and the synthesized patterned sp^2 carbon electrode (c).

Figure 4.6 Characterization of transferred high crystallinity carbon patterns on PDMS substrate. (a, b, f, i) Optical microscopy images of high crystallinity carbon with various pattern shapes. (e) Raman shift collected from the PDMS substrate with (red curve) and without (black curve) high crystallinity carbon pattern respectively. The corresponding G-band (c, g, j) and 2D-band (d, h, k) Raman mapping images collected from b, f, i.

Figure 4.7 Characterization of high crystallinity carbon patterns. (a) SEM image of high crystallinity carbon pattern growth on SiO₂/Si substrate with Ni catalyst. The Ni catalyst was removed by FeCl₃ solution, the surface SEM image (b) shows porous structures. (c) SEM image from cracked carbon patterns indicates the few layer graphene exists in the high crystallinity carbon patterns. (d, e) Optical microscopy images from high crystallinity carbon electrodes with higher resolution, d was clockwise rotated to form e. The corresponding G-band (f), 2D-band (g), and FWHM of 2D-band (h) Raman mapping collected from d.

Carbonized photoresist provides an excellent solid carbon source for the growth of high crystallinity carbon, where the amount of carbon precursor can be precisely controlled by the thickness of the photoresist. In carbonization process, the photoresist concurrently undergoes many chemical reactions such as dehydrogenation and condensation, and finally produced amorphous carbon [30,36,38]. The thickness of AZ 5214 photoresist can be continually controlled from 1.45 μm to 3.24 μm by decreasing the spin rate from 6000 to 1000 rpm. After heat treatment in H_2/Ar atmosphere, the photoresist was converted into carbon films with the volume change of $\sim 85\%$ (**Figure 4.8a**), and the corresponding thickness ranged from 200 to 520 nm (**Figure 4.8b**). The volume change can be calculated by the equation: $(d_{\text{PR}} - d_{\text{C}})/d_{\text{PR}} \times 100\%$, where d_{PR} and d_{C} denote the average thickness of photoresist and carbon films, respectively. Notably, the volume of the photoresist reduced by 85%, this volume change is a constant and not varied by the thickness of original photoresist (**Figure 4.9a**). Although the photoresist was carbonized during annealing, its patterning structure retained, as shown in **Figure 4.5**. AFM height topography shows the geologies of the carbon film, as displayed in **Figure 4.8c-e**. **Figure 4.8d** represents the 3D AFM image of carbon. The surface height profiles (**Figure 4.8e**) were measured by line scans along x, y, and xy direction in **Figure 4d** indicated by the arrows. The results indicate that the photoresist film was totally converted to carbon film with small roughness (~ 0.445 nm in $1 \times 1 \mu\text{m}^2$). **Figure 4.8f, g, h, and i** represent side-view SEM images of the carbon films with the thickness range from 200 to 520 nm, indicating that all carbon films were solidified after carbonization. Also, the sheet resistance of as-prepared carbon films were measured by four-point probe method. The sheet resistance was increased from ~ 130 to $\sim 290 \Omega/\text{sq}$ when the sample thickness decreased from 520 to 200 nm (**Figure 4.8j**). The corresponding conductivity is $\sim 1.6 \times 10^4 \text{ S} \cdot \text{m}^{-1}$, which shows one order smaller than that of high crystallinity carbon patterns. This relatively high conductivity further confirmed the solid carbon film has been successfully synthesized by carbonizing the photoresist.

Figure 4.8 Characterization of the carbon precursor that produced by the pyrolysis of photoresist. (a) Schematic illustration for the shrinkage of pyrolyzed photoresist. (b) The relationship between the thickness of PR and the thickness of carbon precursors. (c) The typical 3D AFM image and the top view optical microscopy image from the carbon electrode, the inset shows the height profile measured by line scanning along dashed line in 3D AFM image, the scale bar in optical image is 40 μm . (d) The surface AFM image of carbon precursor. (e) Height profiles measured by line scanning along X (red curve), Y (yellow curve), and XY (green curve) direction in d respectively. (f-i) cross-section SEM images of carbon films with various thickness. (j) Sheet resistance versus the thickness of carbon films.

Figure 4.9 (a) The thickness of photoresist versus the vertical shrinkage from photoresist to carbon. (b) Schematic illustration for the pyrolysis of photoresist on SiO_2 substrate. The strong interaction between photoresist and SiO_2 substrate makes the lateral geometry size was kept in this pyrolysis process.

The microstructures of carbon films can be fabricated by a conventional photolithography process. Various type of micro-electrodes were designed and produced, including opposite electrodes with the gap of $\sim 5 \mu\text{m}$ (**Figure 4.10a, e**), Hall bar electrodes (**Figure 4.10b, f**), symmetric round electrodes (**Figure 4.10c, g**), and an arm-chair electrode as a heating resistor (**Figure 4.10d, h**). These structures with different geometries can be potentially used for field-effect transistors, Hall devices, antiseptically electronic devices, temperature sensors, as well as measurement of the electrical properties of materials. For example, the Hall bar electrodes was employed to measure the conductivity of high-crystallinity carbon patterns. After carbonization, these photoresist electrodes were converted into carbon electrodes. Their fine structures were perfectly retained after carbonization (**Figure 4.10i-l**). In spite of here shows large volume change ($\sim 85\%$) from photoresist to carbon film, the lateral shrinkage is not observed and finally makes the refined size of photoresist reproduced to the carbon film. I speculate that this is due to the strong interaction between photoresist and the SiO_2 substrate (**Figure 4.9b**), which makes the in-situ pyrolysis of photoresist and results in decreasing the lateral shrinkage while enhancing the thickness change in the vertical direction for mass balance.

Figure 4.10 Various micro-patterned structures for carbon electrode. The schematic illustration of an opposite electrodes (a), Hall bar electrodes (b), symmetric round electrodes (c), and an arm-chair electrode (d). (e-h) The optical microscopy images of micro-patterned photoresist fabricated by photolithography. (i-l) The optical microscopy images of carbon electrodes which pyrolyzed from the photoresist in (e-h).

Ni film is one of the most popular catalysts for the synthesis of high-quality graphene, due to their high solubility for carbon atoms at high-temperature, as well as non-equilibrium segregation during cooling [40-43]. In our experiments, after the thermal treatment of the patterned Ni/C/SiO₂/Si sample, the Ni/C alloy islands were produced along the edges of the carbon precursors (**Figure 4.11**, **Figure 4.12**). I think such Ni/C alloy islands play an important role in translating the geometries of the solid carbon to high crystallinity carbon patterns. **Figure 4.13a** schematically illustrates the growth mechanism of the programmable high crystallinity carbon patterns. At the beginning of growth, the Ni film was covered to the whole substrate with or without carbon precursors. The large thermal

mismatch during the thermal treatment results in the de-wetting evolution between the Ni film and substrate. During the growth of high crystallinity carbon at high temperature, the carbon atoms from the precursors will diffuse into Ni film and form Ni/C alloy. As a result, carbon concentration gradient will be formed at the surface of Ni films and carbon sources because of the thermodynamic equilibrium, where the high concentration carbon atoms aggregate at the surface, and the concentration decrease at the location away from the surface. When it cools down, the high concentration carbon atoms in Ni film will diffuse out and form high crystallinity carbon, while the low concentration carbon atoms in Ni form Ni/C alloy islands. This process is similar to the growth of few-layer graphene. The phenomenon was supported by controlled experiments and complementary characterization including the SEM, EDS mapping, and Raman mapping at the interface between Ni film and carbon precursors (Figure 4.13b, c, d, and g).

Figure 4.11 Optical microscopic images of the samples synthesized with different thickness of Ni catalyst: 100 nm (a), 120 nm (b), 150 nm (c), 200 nm (d), 400 nm (e).

Figure 4.12 (a) Optical microscopic image of the high crystallinity carbon electrode on SiO₂/Si substrate. (b) the corresponding SEM image of carbon electrode. (c) The SEM image shows the boundary of sp² carbon and region of Ni/C alloy.

Figure 4.13 The growth mechanism for the synthesis of micro-patterned high crystallinity carbon films. (a) The schematic illustrates the formation of high crystallinity carbon with the original state, high-temperature state, and final state. (b) SEM image of the interface between the synthesized high crystallinity carbon and Ni film, indicating the Ni/C alloy islands region appears in the interface of the carbon precursor and Ni film, the scale bar is 5 μm. (c) EDS spectra collected from different regions in b, where the dark blue curve for Region I, maroon curve for Region II, and olive curve for Region III. (d) SEM and corresponding EDS mappings of Ni/C alloy islands, the scale bar is 2 μm. (e, f) The optical microscopy image and the SEM image from the sample synthesized by insufficient carbon

precursor, the scale bar in f is 5 μm . (g) The optical microscopy image shows the size of Ni/C alloy regions is not varied with the lateral width of carbon precursors, the scale bar is 50 μm .

The sufficient carbon precursor is crucial for the synthesis of high crystallinity carbon. When the thickness of the carbon film reduced from 402.8 nm to 204 nm, and then followed the same receipt to synthesize high crystallinity carbon. The high crystallinity carbon was only grown at large lateral size carbon precursor region (the line width of $>50\ \mu\text{m}$) because the large line width of carbon precursor provides enough carbon source for growth of high crystallinity carbon. For small size region (the line width of $<50\ \mu\text{m}$), C is not segregated from the Ni/C alloy to form high crystallinity carbon (Figure 4.13e and f). The width of Ni/C alloy islands region is $\sim 40\ \mu\text{m}$, which related to the thickness of Ni film, and irrelevant with the lateral size of carbon precursor. The width of Ni/C alloy islands region not changed when the lateral size of carbon precursor changed from 7 μm to 400 μm (Figure 4.13g, and **Figure 4.14**). Therefore, the carbon precursor preferentially feed to the full Ni/C alloy region, then grow the high crystallinity carbon when reaches the saturation of C in Ni. The high crystallinity carbon sample (the line width of $\sim 1\ \text{mm}$) was scratched to make sure the high crystallinity carbon and Ni film were opened to reveal the covered carbon precursor and substrate (**Figure 4.15**). The interface Raman mapping shows the residual carbon precursor existed under the as-prepared high crystallinity carbon film, which suggesting that the carbon precursor is sufficient in the synthesis of high crystallinity carbon. Therefore, the high-resolution carbon electrode can be achieved by optimizing the thickness of carbon precursors via photoresist. The line width and channel gap of graphene can reach of $\sim 2\ \mu\text{m}$.

Figure 4.14 (a, b) Optical microscopic images of the high crystallinity carbon with different geometries on SiO_2/Si substrate, the Ni catalyst was not removed. (c) the width of Ni/C alloy region versus the width of precursor, which indicates the width of Ni/C alloy region not increased/decreased when the lateral size of carbon precursor changed.

Figure 4.15 (a) The optical microscopy image, (b) the 2D-band, and (c) G-band Raman mappings from high crystallinity carbon and carbon precursor, where the high crystallinity carbon located at the top of carbon precursor. (d) Raman spectrum collected from the high crystallinity carbon (upper-left in a) and carbon (lower-right in a).

The as-grown high crystallinity carbon patterns were transferred to flexible substrate such as PDMS and PET to evaluate its performance as a flexible electronic device. The translucent flexible device was obtained due to the micro-patterned structures (**Figure 4.16**). The fabricated device was attached to PET substrate which can be used to conduct the positive bending and negative bending. **Figure 4.17a** illustrates two cases for bending test using α , the bending angle: $\alpha < 180$ denote the positive bending and $\alpha > 180$ denote the negative bending. The positive bending will produce compressive strain in carbon film, while negative bending leads to tensile strain. Interestingly, the electrical resistance of high

crystallinity carbon is slightly changed under positive bending, but remarkably changed under negative bending (Figure 4.17b). This carbon-based device shows promising for the mechanic-based rectifier to detect the bending direction. The rectification ratio is 143, which can be defined as the resistance of negative bending divided by the resistance of positive bending at $180^\circ \pm 60^\circ$. In Figure 4.17c, the measured resistance (R) is normalized with original resistance (R_0) to illustrate the variations, $\sim 10\%$ variation was observed when the high crystallinity carbon was bended from 180° to 0° (the curve radius is around 4 mm at 0°), which makes it an electrode material for the applications of flexible device. For the negative bending, the carbon-based device is very sensitive to the tensile strain due to cracking mechanism [44, 45]. The failing angle is larger than 260° . Therefore, the high crystallinity carbon film under the situation of negative bending provides an opportunity to construct high-sensitive mechanical sensors such as vibration sensors, pressure sensors and flexion sensors. As shown in Figure 4.17d, the vibration sensor was demonstrated under negative bending. Our flexible carbon-based device is capable in monitoring the vibrations from phone timer. It is notable that the device shows a very fast response time (~ 10 ms) and excellent reproducibility. As illustrated in the inset of Figure 4.17d, the second vibration (blue curve) is almost coincident to the first vibration (red curve). To figure out why our device is sensitivity to the bending direction, the optical microscopy was employed for in-situ characterization of the strained high crystallinity carbon film. The 3 LED lights were series connected to the device for visually showing the electrical conduction or not. The initial state shows in Figure 4.17f (corresponding to point iii in Figure 4.17b), the high crystallinity carbon film presents wrinkle structures like human skin, which enable it to resist to large deformation. Despite the small cracks and defects were formed at the surface, the lit LEDs indicate that the electronic conductivity of high crystallinity carbon has not changes a lot, in good agreement with in Figure 4.17b. When negative bending is applied, the tensile strain was applied to high crystallinity carbon film, where the wrinkle will be straightened and the cracks will be amplified. Finally, the cracks propagate and make the high crystallinity carbon film electrical insulated (the LEDs light off), as shown in Figure 4.17e, which is corresponding to point vi in Figure 4.17b. When positive bending was conducted with the bending angle of $\sim 103^\circ$ and $\sim 0^\circ$ (point i and ii in Figure 4.17b), a huge amount of wrinkles were produced by the surface compression of

high crystallinity carbon. This compressed carbon shows electrical conducting (lit LEDs) because the wrinkle structures haven't destroyed the carbon by bring the new fractures. The Hall device indicates the high crystallinity carbon film has a conductivity of $\sim 1.96 \times 10^5 \text{ S} \cdot \text{m}^{-1}$ and a sheet resistance of $\sim 51 \Omega/\text{square}$ at room temperature (Figure 4.18). The value of conductivity is one order higher than that of amorphous carbon precursor film ($\sim 1.6 \times 10^4 \text{ S} \cdot \text{m}^{-1}$) due to the structure ordering of carbon atoms in high crystallinity carbon pattern. The high conductivity makes it promising as the electrode material for flexible electronics.

Figure 4.16 Photograph of micro-patterned high crystallinity carbon electrodes on PDMS substrate, which shows the device possess translucent and flexible properties.

Figure 4.17 The carbon-based bendable electronics. (a) The schematic illustrates the two bending conditions: the positive bending and negative bending. (b) Devices resistance versus different bending angles, where the positive bending denoted by the bending angle from 0° to 180° , and the negative bending indicated by the bending angle from 180° to 360° . (c) The resistance change of bendable carbon device under positive bending. (d) The high-sensitive vibration sensor was demonstrated at negative bending. (e-h) Photographs and in-

situ optical microscopy images for different bending conditions, corresponding to the point vi, iii, ii, and i in b, respectively. The scale bar is 200 μm .

Figure 4.18 (a) Optical microscopic image of high crystallinity carbon-based hall device. (b) The I-V curves from each pair of electrode in a. The table represents the conductivity of high crystallinity carbon calculated from different electrode couples.

4.4 Conclusions

In summary, a new method for the synthesis of high-quality and programmable high crystallinity carbon micro-patterns was developed, using solid carbon precursors prefabricated by carbonizing photoresist. More importantly, this process is compatible to conventional photolithography, which makes it easy for large-scale fabrication of carbon-based devices. The high crystallinity carbon patterns can reach the resolution as high as $\sim 2 \mu\text{m}$, which meets the requirement of most flexible electronics. The carbon-based bendable electronics have been demonstrated by transferring it to a flexible substrate, which presents

relatively high stability under positive bending and ultra-sensitive to sense the deformation at negative bending. The tunable electrical properties enable the carbon-based device to be amazing and promising for the construction of the new type of flexible and bendable electronics.

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Chapter 5

Self-crosslinked Carbon Arrays

Carbon nanomaterials provide a new realm of opportunities for the next generation of electronics. Currently, materials such as carbon nanotube (CNT), graphene and graphene derived materials (e.g. graphene foam and reduced graphene oxide) have been studied and synthesized by researchers for flexible electronics. Here, a novel carbon nanomaterial that is characterized as a self-crosslinked carbon array (CA) was reported, where an individual unit is the intermediate state between the CNT and carbon nanofiber (CNF). Its applications in flexible sensing electronics were demonstrated. The unique nanostructures in the CA such as self-crosslinked points and vertically aligned nanorods reduced the residual stresses, making the CA-based flexible device possess high sensitivity and good stability (~10,000 times) in the detection of flexions. The results show that the 3-dimensional (3D) structure of the self-crosslinked nanorod arrays is far more superior to 2-dimensional (2D) networks and solid thin films in avoiding the growth of mechanical cracks during the duration of application of the flexible electronics. CA-based flexible devices can record low frequency vibrations (<6 Hz). As such, the CA-based flexible device's capabilities in monitoring the rest tremor of human body was demonstrated, which is an initial symptom of Parkinson's disease. The findings in this report indicate that the self-crosslinked CA is a promising flexible sensing electronic device and they showcase the device's potential as a cost-effective flexible sensor for early diagnosis of disease by monitoring the health-related rest tremors.

5.1 Introduction

Since the early 1990s, one-dimensional (1D) carbon nanomaterials such as carbon nanotube (CNT) and carbon nanofiber (CNF) have attracted a copious amount of attention due to their unique electrical and mechanical properties, such as good mechanical flexibility, high optical transparency, and tunable electrical properties [1-5]. 1D nanomaterials are mostly assembled to wafer scale for device fabrication [6,7]. Several methods have been developed to assemble 1D nanomaterials to form network film. These include wet chemical assembly process and direct growth method through chemical vapor deposition (CVD) with dry transfer [8-15]. However, most of the contact points between the nanotubes/nanofibers are only bonded physically, resulting in contact resistance at the interface and in turn casting a shadow on the electrical stability and reliability of the material upon repeated bending and when used in flexible electronics [14]. To eliminate the negative influence from contact resistance, scientists have developed aligning and welding methods to reduce the contact points and contact resistance of network films [16-19]. Nevertheless, new methods and technologies still need to be developed because the aforementioned methods are only available for specific materials and architectures.

Current studies have established the carbon based nanomaterials (e.g. CNT and graphene) as great candidates for flexible mechanical sensors such as flexible pressure and strain sensors [20-23]. These flexible sensors have shown their capabilities in monitoring the health related physiological signals such as heart rate, blood pressure, and wrist pulse [21,24,25]. Therefore, such sensors can be used for wearable health monitoring, which is a convenient and non-invasive way for disease pre-diagnosis and health assessment. However, most of the current flexible sensors are limited to track cardiovascular and blood diseases. To the best of our knowledge, the monitoring of Parkinsonian tremor by flexible/wearable sensors is quite rare, although Parkinson's disease is vastly prevalent in the current ageing society [26]. In this work, 3D self-crosslinked carbon arrays (CA) were synthesized, and subsequently be demonstrated in flexible sensing electronics for the detection of Parkinsonian tremor. The 3D self-crosslinked CA is composed of a new type of carbon materials which is an "intermediate" form between the CNT and CNF. The self-crosslinked structure enhances the contact points between individual carbon units and

eradicates the electrical instability by reducing the residual stresses in the material. The CA-based flexible sensors show high sensitivity and good stability (~10,000 times) in the detection of flexions and low frequency vibrations (<6 Hz), and are capable of monitoring the Parkinsonian tremor.

5.2 Experimental Methods

5.2.1 Synthesis of self-crosslinked carbon arrays and characterization.

The CVD method with CH₄ precursor and Ni catalyst was employed to synthesize self-crosslinked carbon arrays. Firstly, the 5 nm Ni catalyst on SiO₂/Si substrate was fabricated by E-beam deposition with the working voltage of ~4.99 kV and the current of ~90 mA. The micro-patterned Ni catalyst can be achieved by traditional photolithography process. Then, the prepared SiO₂/Si substrate with 5 nm Ni catalyst was set into the center of quartz tube furnace. For flushing and removing the residual air in tube, the H₂ gas was inlet into it for 15 minutes. The mechanical pump was linked to quartz tube for pumping until the pressure down to ~1.5 mBar. Then, the furnace was heated to 900° and kept for 15 min at 900°. In heat preservation process at 900°, the gas vent keep closed and the pure CH₄ gas was inlet into the furnace with strictly controlled flow rate of 10 sccm. In this process, the pressure was gradually increased from ~1.5 mBar to ~155 mBar in 15 min. After that, the CH₄ gas was switched to pure H₂, and the furnace was cooling down to room temperature. Finally, the carbon nanorods array was grown onto SiO₂/Si substrate, and followed geometries of Ni catalysts. The prepared samples were characterized by SEM (JEOL 6340), TEM (JEOL 2010HR, JEOL 2100F), XRD (Bruker D8 Advance), and Raman (WITec alpha300 RAS Raman system).

5.2.2 Fabrication of Flexible Sensing Electronics and Performance Evaluation.

The prepared CA was transferred to target flexible substrate such as PET and PDMS for device fabrication. The CA can be lift off from SiO₂/Si substrate by etching SiO₂ layer using HF solution. The edge of prepared CA materials on SiO₂/Si substrate was cut to make

sure the SiO₂ layer bared to environment, and immersed it to HF solution for ~12 h. The SiO₂ layer will be etched from the edge to the center of materials, finally the CA floated onto the surface of HF solution. The PET film and PDMS film were used to transfer the floated CA by immersing them in HF solution. Then, the CA with PET (or PDMS) was rinsed by DI water several times for removing the residual HF. The Cu wires with Ag paste were connected to each terminal of CA materials to form resistance sensors. The semiconductor device analyzer (Agilent 1500B), and Lab VIEW controlled digital source meter (Keithley 2450) were used to measure the resistance change of devices in real-time. The homemade linear stepper stage with the resolution of 10 μm was used to load the bending to device, and the digital camera was employed to measure the bendable angles and derived heights.

5.3 Results and Discussion

5.3.1 Characterization of Carbon Arrays

The self-crosslinked CA was synthesized by CVD method at high temperatures (~1000°C) and dynamic change of pressure, using CH₄ as the carbon precursor. In the growth process, the pressure is dynamically changed within the range of ~1.5 m bar to ~160 m bar by controlling the amount of reaction gases added. 5 nm Ni film on SiO₂/Si substrate was used as catalyst to grow CA because the Ni has a great ability to dissolve carbon, and it has been proven as a good catalyst for the growth of CNT [27-30]. In this experiment, the pressure change is the crucial parameter to ensure the production of CA instead of CNT. As displayed in **Figure 5.1a**, the self-crosslinked CA is a microstructured thin film, and it composes of carbon nanorods (CNRs) which are terminated by Ni/C particles and crosslinked to each other to form the thin film. The interlaced points between individual carbon materials serve as an electronic channel that permits electrical conductivity. The CNR has a different structure as compared to CNT. Figure 5.1b schematically illustrates the structure difference between CNR and CNT.

Figure 5.1 Schematic structure of self-crosslinked carbon arrays and characterizations. (a) Schematic illustration of self-crosslinked carbon arrays. (b) The cross section simulation of the CNR and CNT, suggesting that the individual unit of CA is different than that of CNT and that it is an intermediate state between the CNT and carbon nanofiber. Top view (c, d,) and side view (e) SEM images of self-crosslinked CA show the individual unit vertically aligned to the substrate and crosslinked to each other. The contact points between the individual units are strong chemical bonds instead of the physical stacking interactions. (f) A typical Raman shift of the sample shows the amount of defects that exist in the prepared CA. (g) XRD pattern shows a wide and weak peak at 25.1°, which indicates a layered structure with the interlayer spacing of ~0.35 nm in CA. (h, i, j) TEM images of CNRs connected with chemical bond (h, j) and physical bond (i) respectively.

Figure 5.2 TEM characterisation of CNR and CNT. (a) Cross section simulation of CNR. (b) TEM image of CNR with Ni catalyst. (c) HRTEM images from the marked areas in b. (d) Cross section simulation of CNT. (e) TEM image of CNT with Ni catalyst. (f) HRTEM images from the marked areas in e, scale bar is 5 nm in c and f.

There are two characteristics that distinguishes the CNR from CNT: i) the solid and layered carbon atom packing (without inner hollow and tubular structure unlike CNT); ii) the carbon layer that tightly covers the whole Ni catalyst different from the partial cavity at the outside of the Ni catalyst in the CNT (**Figure 5.2, Figure 5.4**). The photographs and the top view SEM image indicates that large scaled, uniformed, and high quality CNR arrays have been synthesized (Figure 5.1c-d). The side view SEM image shows the length/diameter (L/D) ratio of the CNRs to be around 10. It also shows that the CNRs are approximately vertical and incline to the substrate (Figure 5.1e) and are interlaced. With our method, the L/D ratio of CNRs lies in the range of 8 to 20 and can be readily controlled by the reaction time (to be discussed later in the part of growth mechanism). The typical Raman shift of the sample is shown in Figure 5.1f, and displays the strong and wide D-band at $\sim 1354\text{ cm}^{-1}$ and G-band at $\sim 1590\text{ cm}^{-1}$. It is difficult to observe the 2D-band around 2700 cm^{-1} . This results in a small intensity ratio of 2D band to G band, which suggests that the prepared CNRs possess weak crystallinity and a lot of defects. The XRD pattern shows a wide and weak peak at 25.1° but a strong Si (200) peak at 32.9° , indicating that a layered structure with the interlayer spacing of $\sim 0.35\text{ nm}$ exists in the CNR arrays. The interlayer spacing of the material can be established by Bragg's law and its value is close to the interlayer spacing of graphite and multi-wall CNTs [31-34].

To investigate the inner microstructures of as-prepared carbon nanomaterials by TEM, the carbon nanorods on SiO_2/Si substrate were scraped from the substrate and dispersed in ethanol solution. The solution was then dropped to a carbon filmed copper grid and dried for TEM characterization. **Figure 5.3a** shows the typical TEM image of a single CNR. Notably, it is different from CNT with the tubular structure not observed from our carbon nanomaterial. The black region in Figure 5.3a is the Ni catalyst which is covered by the carbon layers. Figure 5.3b shows the high resolution TEM (HRTEM) image of the carbon layers on Ni catalyst (the white dashed box in Figure 5.3a), which has a thickness of $\sim 43\text{ nm}$ (110-130 layers). The fingerprint-like structure suggests that the layered structure existed in carbon materials. I believe that these carbon layers suppressed the Ni catalyst and eliminated the growth of longer carbon nanorods, which is similar to the mechanism of the Ni catalyst growth of multi-walled carbon nanotubes [29,30]. Figure 5.3c presents the HRTEM images of the edge region of a carbon nanorod (as marked with the dark

dashed box in Figure 5.3a). The carbon layers can be clearly observed by the dark and white fingerprint lines which have a layer spacing of ~ 0.36 nm that is close to, but slightly larger than, the interlayer spacing of graphite and carbon nanotube [33,34]. The carbon nanorod was made up of multiple carbon layers. The discontinuous and crooked fingerprint lines in the HRTEM image indicates that each layer of the carbon nanorod is filled with the defects, as shown in Figure 5.3c-i, ii, and iii. Generally, the HRTEM image of multi-walled carbon nanotubes presents distinguishing and straight fingerprint lines [35] (**Figure 5.5**). Therefore, the amount of defects is one of the important characteristics for distinguishing the CNR from CNT. The abundant defects in the CNR may endows it with different kinds of mechanical and electrical properties, such as increased tensile strength and modified electron transport behavior because of the quasi-one-dimensional geometry [36,37].

Figure 5.3 TEM characterization of the individual CA units. (a) Low-magnification TEM image of a single carbon nanorod shows the Ni catalyst located in the center of one terminal and fully covered by the carbon layers. (b-c) High-resolution TEM images observed from the marked squares in a, b is the image corresponding to the marked white square, and c corresponding to the marked gray square. i, ii, iii, are magnified HRTEM images from the marked regions of c respectively, indicating the discontinuous and crooked carbon layer stacking and the abundant defects.

Figure 5.4 HRTEM image of carbon layers coated Ni catalyst, indicating the carbon layers fully covered the Ni catalyst.

Figure 5.5 HRTEM images of CNR (a) and CNT (b), scale bar is 2 nm. CNR shows more defects than CNT, which make the carbon layers of CNR less distinguishable and straight than that of CNT in HRTEM images.

5.3.2 Growth Mechanism of Carbon Arrays

The CVD method (with CH_4 gas as the carbon precursor and Ni catalyst) was employed to synthesize CNR arrays at high temperature with a dynamic change of pressure. According to chemical thermodynamics, CH_4 will decompose into solid carbon and H_2 at high temperatures because the Gibbs free energy of solid carbon and H_2 are lower than that of CH_4 at the same environment. Previous research has demonstrated that the pyrolysis of CH_4 in a flow reactor (such as tube furnace) belongs to the first-order reaction, with the reaction rate constant and the activation energy being $\lg k(\text{s}^{-1}) = (13 - 18.6) \times 10^3 / T$ and $E_a = 356 \text{ kJ} \cdot \text{mol}^{-1}$ respectively [38]. At the early stages of the high temperature reaction, the CH_4 gas produces aromatic compounds which have higher molecular mass and lower Gibbs free energy. The Gibbs free energy of most aromatic compounds is lower than that of CH_4 at the temperature range of 1100°C to 2000°C [39]. As such, the compounds will gradually thermo-decompose into carbon [40]. However, the pyrolysis mechanism of CH_4 in our experiment was different than that of the above process. The CH_4 gas directly decomposed into carbon and H_2 instead of aromatic compounds due to the relative low reaction

temperature (900°C). As shown in inset of **Figure 5.7a**, the Gibbs free energy of CH₄ is lower than that of aromatic compounds at the temperature of 900°C, suggesting that the aromatic compounds are thermodynamic non-equilibrium in this situation [39, 41]. The 5 nm Ni catalyst film was heated to generate liquid Ni nanoparticles when the temperature reached 900°C. Then, CH₄ gas was introduced into the tube furnace which subsequently decomposed into carbon atoms which was absorbed by Ni catalyst to form Ni/C alloy. When the concentration of carbon exceeds the saturation concentration in Ni/C alloy, the carbon atoms separate out from the Ni/C alloy to form solid carbon (**Figure 5.6**). The HRTEM images taken from the interface of the Ni catalyst and carbon layers is displayed in Figure 5.7d-f. These images clearly show the carbon layers and the (111) lattice plane of the Ni catalyst. The carbon layers are almost parallel to the Ni (111) lattice plane, which suggests that the carbon atoms were separated from alloy along the Ni (111) lattice plane, which is the same process in the growth of CNT and graphene by the Ni catalyst [42-44].

Figure 5.6 Schematic illustration for growth mechanism of CNR.

Figure 5.7 Growth mechanism of self-crosslinked carbon arrays. (a) Schematic illustration for growth mechanism of CA. Inset: Gibbs free energy of various hydrocarbons as a function of temperature. (b,c) TEM images of CA observed from the outside interface of individual units, which show the defects at the outmost carbon layers. (d,e) HRTEM images observed from the interface of the Ni catalyst and carbon layers. (f) Re-structured simulation for the interface of Ni and carbon layers. The carbon layers are parallel to the Ni (111) lattice plane, suggesting that the carbon atoms were separated from alloy along the Ni (111) lattice plane in the growth process. (g) The diameter of the individual unit of

the CA with the reaction time. (h) SEM images of the materials synthesized by different reaction times.

Due to the weak hydrophilicity between the liquid Ni/C nanoparticles and the SiO₂/Si substrate, the liquid nanoparticles will lift off from the substrate by the synergistic effect of the saturated carbon nanorods. The defects in the carbon layers possess high chemical energy for the absorption of decomposed carbon atoms and hence, act as the active site to grow carbon nanorods layer by layer. The defects bring about the stacking fault, and trigger a mass of defects in final product (Figure 5.3c). The synthesized CNR samples with different reaction times indicated that the average diameter of CNRs was significantly increased when the reaction time was prolonged, while the length of CNRs were not changed (Figure 5.7g-h). This phenomenon is different than the growth of CNTs, where the length of the nanorods were changed with the reaction time, but the diameter was determined by the size of the catalyst [27, 29, 45]. This result further demonstrates the defects in the outmost carbon layers that are crucial in growth of CNRs.

5.3.3 Carbon Arrays for Bendable and Vibration Sensors

The prepared CNR array was transferred to flexible substrates such as PET for resistance-type sensors. As shown in **Figure 5.8a**, two clamps driven by the high-resolution stepping motor was employed to clamp down the device with varying step distances (Δx). The bendable angle (α) and derived height (d) were used to quantify the bend behavior, where α and d gradually increased when the bending intensified as increasing the step (from i to iv). In order to eliminate the size effect of our devices, the ratio of derived height (d) over device length (L) was used to describe the bend behavior. When the step distance was linearly increased, the ratio of d/L and bend angle (α) showed similar non-linear behaviors, where the ratio of d/L trend to the value of 0.5 and the bend angle (α) trend to 90° respectively (Figure 5.8b).

Figure 5.8 Carbon arrays based flexible sensors for the detection of flexion and low frequency vibrations. (a) Schematic illustrations and optical graphs of PET substrate with CA materials under different bending conditions. (b) The ratio of d/L (the derived height over device size) and bendable angles with the ratio of $2\Delta x/L$ (the step distance over device size). Inset shows the overlapped optical graphs of device with different bending conditions. (c) The sensitivity of device with various materials under different bending conditions. (d) The resistances of device under different bend conditions. (e) Real-time I-t curve of CA device with various bending circles. (f) Schematic illustration of damping vibrations generated by PET substrate, where the CA-based sensor was set on its surface. (g) Real-time current response of CA-based sensors to damping vibrations. (h) The real-time I-t curve was processed by Fast Fourier transform (FFT), which indicates that the dominant frequency of this damping vibration is ~ 5.5 Hz. (i) The polar coordinate of the current intensity changes.

The resistance change of the device was measured using different bend angles from 5 ° to 88 ° achieved by bending with the ratio of d/L from 0.002 to 0.595, corresponding to the derived height from 2 to 20 mm. The resistance sensitivity S is defined as the normalized resistance change, $S=(R-R_0)/R_0 \times 100\% = \Delta R/R_0 \times 100\%$, where R is the resistance of the device when bended and R_0 is the resistance when the device is relaxed. The sensitivity of the device at different bend angles and the real-time resistance sensitivity are displayed in Figure 5.8c and d respectively. Notably, the resistance sensitivity of the CNR device increased gradually as the bending increased, and it shows a linear relationship with the ratio of $2\Delta x/L$. The real-time resistance sensitivity curve indicates that the CNR device repeatedly gave a fast response to the external simulation of bending. More importantly, the signals recovered promptly (<1 s) to the original baseline value upon the relaxing of the device. The performance of CNR based device was compared with amorphous carbon film, high crystallinity carbon film, Ag network, and CNT network based devices (Figure 5.8c) [23,46]. It can be seen that the CNR based device has the highest sensitivity, the best stability and reproducibility, as well as the largest tolerable detection range as compared to the other devices. To investigate the stability of CNR device, the sample was bended more than 10,000 times, with a bend angle of $\sim 45^\circ$ and 3 s per cycle. The device showed good stability with only a minor resistance change ($\sim 20\%$). I think this resistance change can be reduced by encapsulation in real applications. To investigate the changes in microstructure of materials, the optical microscopy was installed onto homemade moveable stage for in-situ characterization of materials upon bending (**Figure 5.9**). The CNR film presents better mechanical property than solid film. The few cracks (with the density of <1 crack/100 μm) were observed in CNR film, while a mass of cracks (with the density of ~ 15 cracks/100 μm) existed in bended solid films. I believe the self-crosslinked points and vertically aligned individual nanorod unit in CNR film reduced the residual stresses, which avoid the mechanical cracking when bend, and making the CNR-based flexible device possess superior structural stability to solid film.

Figure 5.9 In-situ characterisation on bending test. (a, b) Experimental setup on in-situ characterisation by optical microscopy and homemade moveable stage. The bend angle from 0 to 90. (c) Schematic illustration of bending test for solid film, i and ii are optical microscopy images of solid film with and without bend respectively. (d) Schematic illustration of bending test for CA film, i' and ii' are optical microscopy images of CA film with and without bend respectively. All scale bar is 100 μm in c and d.

The CNR based device can also act as a mechanical sensor to detect vibrations. As an example, damping vibration was generated by bending and freely relaxing the device on a PET substrate, wherein one of the terminals was fixed and the other was kept free (Figure 4f). The damping vibration test can be simulated on the PET substrate due to its big Young's modulus ($\sim 2\text{-}4$ GPa) and suitable elasticity. As such, the up and down "spring like" movement of the PET substrate induced strain and pressure to the CNR material. The real-time current changes of the device were recorded throughout the entire damping vibration process, as displayed in Figure 4g. When the device was bent downwards, the current significantly decreased. Subsequently, the current fluctuated in response to the vibration and eventually as the damping vibration stopped, returned back to the original baseline. The real-time I-t curve depicted in Figure 4g was processed by the Fast Fourier transform (FFT) technique, and the frequency data obtained is shown in Figure 4h. The fitted curve (blue line in Figure 4h) indicates that the dominant frequency of the damping vibration process is ~ 5.5 Hz. Our CNR based flexible sensor presents high sensitivity for detection and recording the damping vibration with a frequency of ~ 5.5 Hz. In Figure 4i, the polar coordinate was established to describe the current intensity changes of the device, where the average half maximum was defined as the current intensity and $2s$ was defined as one period of polar coordinate. The results showed that the current intensity spirally decreased to the center of the coordinate, which denoted the current base point of device. The current intensity change in this polar coordinate shows a similar behavior to the traditional amplitude change in the damping vibration, suggesting that the CNR based flexible device is capable of the detection of damping vibration.

5.3.4 Carbon Array Flexible Sensors for Monitoring the Parkinsonian Tremor

The CA based flexible sensor can be used to monitor the health related physiological signals such as rest tremor, which is a symptom of neurological disorder. For example, Parkinsonian tremor shows pill-rolling action of the thumb, and is often a precursor to Parkinson's disease (**Figure 5.10a**). The CA flexible device was attached to the human hand near the adductor pollicis, and an iPhone6 equipped with a commercial sensor was

used as a referenced sensor (Figure 5.10b). The Parkinsonian tremor was simulated by vibrating the hand and thumb. The real-time I-t curve of the CA device and the real-time signal from the iPhone6 sensor fully recorded the simulated tremors, as displayed in Figure 5.10c. Both signals were processed by Short-Time Fourier transform (STFT), and the processed image of time & frequency of the CA device has a high concordance with the reference sensor of the iPhone6 (Figure 5.10d). The CA based flexible sensor showed high sensitivity and good reliability in monitoring the simulated tremors. The results indicate that the performance of the CA flexible sensor is comparable to the referenced commercial sensor, which is produced by micro-manufacture technology at high-costs. The CA based flexible sensor paves the way for low-cost flexible health sensors that can be used for health monitoring.

Figure 5.10 Monitoring the Parkinsonian tremor by CA-based flexible sensors. (a) Schematic illustrations of the Parkinsonian tremor. (b) The CA-based flexible sensor and reference sensor of the iPhone6 were placed on the human hand to monitor the simulated

Parkinsonian tremors. Real-time responses (c) and Short-Time Fourier transform (STFT) processed signals (d) of our flexible sensor and referenced sensor, indicate that the performance of cost-effective CA-based flexible sensor is comparable to the reference commercial sensor.

5.4 Conclusions

In summary, 3D self-crosslinked CA was prepared, and its applications in flexible sensing electronics were demonstrated. This novel carbon nanomaterial is far more superior to 2D networks and solid thin films in the application as flexible electronics, and shows high performance in the detection of flexion and low frequency vibrations (~6 Hz). These include high sensitivity, low power consumption as well as good stability and reliability. These contributions enable the 3D self-crosslinked CA to be a promising tool in the pre-diagnosis of Parkinson's disease by tracking the diagnostic rest tremors. This study paves the way for the wearable health monitoring system and seeks to propel the traditional disease diagnosis for Parkinson's disease towards cost-effective telemedicine.

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Chapter 6*

Vertical Piezoelectricity from CdS ultrathin Films

Piezoelectric materials are promising in both applications of accurate pressure/strain sensors and actuators. In this chapter, an important piezoelectric material, CdS ultrathin films were developed, and their piezoelectricity was fully investigated. Using ultra-thin CdS thin films, this chapter demonstrated the giant vertical piezoelectricity in atomic scale (3~5 space lattices). By employing an in-situ scanning kelvin force microscopy, single and dual-frequency resonance tracking piezoelectric force microscopy, the vertical piezoelectric coefficient (d_{33}) up to $33 \text{ pm}\cdot\text{V}^{-1}$ has been determined for the CdS ultra-thin films. These findings will shed light on the design of next-generation sensors and micro-electromechanical devices.

*This section has been published substantially as: “**Xuewen Wang**, Xuexia He, Hongfei Zhu, Linfeng Sun, Wei Fu, Xingli Wang, Lai Chee Hoong, Hong Wang, Qingsheng Zeng, Wu Zhao, Jun Wei, Zhong Jin, Zengxiang Shen, Jie Liu, Ting Zhang, Zheng Liu, Subatomic Deformation Driven by Vertical Piezoelectricity from CdS Ultrathin Films, *Science Advances*, **2016**, 2, e1600209.”

6.1 Introduction

Piezoelectric material has proven to be a key to achieve high resolution positioning, which is crucial for fundamental research and industrial applications. Recent work on piezoelectricity of two-dimensional materials provide the opportunities for constructing thin electromechanical coupled devices, such as nanoscale mechanical transducer and micro-energy system [1-3]. Due to the break of centrosymmetry in monolayer crystals, only a few 2-D layered materials (including graphene, h-BN, C_3N_4 , $2H-ACh_2$, where $A=W$, Mo ; $Ch=S$, Se , Te) have been predicted to possess piezoelectricity [4,5], which has been exemplified in few layered MoS_2 based flexible and suspended devices [1,2,6]. In these work, in-plane strain was produced by AFM tip (or flexible substrate) on the films, which resulted in charge aggregation when applied a lateral bias to the materials (**Figure 6.1**). However, these methods can be only employed to study the in-plane piezoelectricity, such as d_{11} and d_{22} , although the vertical piezoelectric coefficient (d_{33}) is the key parameter to evaluate the performance of piezoelectric materials.

Figure 6.1 Schematic illustration of local characterization of in-plane piezoelectricity and vertical piezoelectricity. In-plane piezoelectricity (d_{11} , d_{22}) of ultra-thin materials is the planar electromechanical couple behavior, where the applied stress and produced piezoelectric potential are located at the in-plane of exposed lattice plane. Vertical piezoelectricity (d_{33}) focus on electromechanical interaction occurred in vertical axis, which is perpendicular to the surface of materials. The high-precision deformation actuator can be implemented using accurate positioning the materials surface by vertical invert-piezoelectricity.

For intrinsic piezoelectric materials, the vertical symmetry breaking still remains even for thin films down to a few layers of atoms. Therefore, theoretically, the vertical piezoelectricity (d_{33}) can be obtained from ultra-thin piezoelectric materials such as ZnO, CdS, and CdSe nanoplatelets. In this case, when the stress is applied to such ultra-thin piezoelectric materials toward out of plane, the geometric deformation will generate negative and positive charges simultaneously. These charges will distribute at the top and bottom surfaces under the external bias (**Figure 6.1**). However, synthesis of the ultra-thin piezoelectric materials is the main challenge to determine the vertical piezoelectricity (d_{33}). Up to now, just a few works reported the synthesis of atomic thin piezoelectric materials by wet chemical method, such as ZnO, CdS, and CdSe nanoplatelets [7-10]. Although these achievements present valuable advances, many critical problems remain and limit their applications. For instance, due to organic solutions that were used for synthesizing CdS, the remaining organic molecules at the surface of CdS may cast shadows on the piezoelectricity of CdS. In this chapter, using chemical vapor deposition, the CdS thin films down to 2~3 nm was synthesized. The vertical piezoelectricity d_{33} of CdS in atomic scale (3~5 space lattices) was demonstrated by single and dual-frequency resonance tracking piezoelectric force microscopy (DART-PFM). The surface potential and charge distribution were measured by scanning kelvin force microscopy. The vertical piezoelectric domains at the CdS thin films were observed, and the measured piezoelectric coefficient (d_{33}) was $32.8 \text{ pm} \cdot \text{V}^{-1}$. The value was ~3 times larger than that of the bulk CdS. In addition, the contact PFM process could largely change the surface potential of CdS thin film by producing the charges at its surface. These works will shed light on the vertical piezoelectricity of ultrathin (lattice scale) nanomaterials, and promote their applications in actuators with a sub-atom resolution.

6.2 Experimental Methods

6.2.1 Growth of CdS Thin Films.

Synthesis of ultra-thin CdS nanoplatelets was carried out in a conventional tube furnace (Thermal Fisher, Lindberg/Blue MTF55035C-1). The experimental setup is shown in **Figure 6.2**. A tube furnace equipped with a 1-in. quartz tube and connected to Ar gas inlets. The starting materials were sulfur (1 g) and Cd grain (60 mg), which were placed in different porcelain boats inside the quartz tube. The Si/SiO₂ substrates (230 nm SiO₂ on Si) were placed downstream of Cd grain, and the center of the furnace to collect the products. Then, the system was flushed with argon flow (100 sccm) for more than 3 cycles, and heated to the targeted temperature of 600 °C with a rate of 20 °C/min. When the temperature reached and kept in targeted temperature for 30 min, the furnace was instantly switched off and was cooled down to room temperature naturally. Finally, the CdS thin films were grown on the Si/SiO₂ substrate.

Figure 6.2 Growth of CdS thin films. (a) Schematic of synthesis of CdS thin films by CVD. The system was flushed with ultrahigh purity Ar gas with 100 sccm flow rate for 3 cycles, and heated up to 600 °C with a rate of 20 °C/min⁻¹, and kept 30 min for growth of CdS ultra-thin films. (b, c) Typical optical images of as prepared CdS ultra-thin films with

different morphologies, showing that high quality CdS samples were synthesized over large area.

6.2.2 Fabrication of FET Device and Calculation for Carrier Concentration

The FET device was fabricated by conventional photolithography process as follows: firstly, a layer of $\sim 2 \mu\text{m}$ photoresist (AZ5214E, photoresist image reversal, MicroChemicals GmbH) was spin-coated to the CdS thin films at Si/SiO₂ substrate at 3000 rpm for 30 s, and then pre-baked at 105 °C for 2 min. The alignment was adjusted by microscopy to make sure that CdS sample was located between the source and drain. The source and drain patterns were subsequently transferred from the photolithography plate to a CdS sample by exposing to UV light for 4 s at $\sim 44 \text{ mW cm}^{-2}$ (SUSS MicroTec, MJB4) and developed for 30 s (AZ Developer : H₂O = 1 : 1, AZ Electronic Materials GmbH). Then, Ti/Au (30/150 nm) films were deposited by electron beam evaporation (Edwards Auto 306). The microelectrodes were finally formed by a lift-off process.

6.2.3 Characterization and 3D FE Simulation.

Both Raman and PL data were collected at room temperature using 457 nm laser as an excitation source (WITec alpha300 RAS Raman system). The sample size, thickness, morphologies, surface potential, and vertical piezoelectricity were conducted by optical microscopy (Olympus BX51), AFM, SKFM, PFM, and DART-PFM (Cypher S, Asylum Research). The AFM and SKFM were conducted at AC mode and nap mode, while PFM and DART-PFM were conducted with contact mode. The PFM was employed as conductive tips of Pt/Ir coating, and with the force constant of 2.8 N/m. The resonance frequency is $\sim 75 \text{ kHz}$ for non-contact mode, and $\sim 350 \text{ kHz}$ for contact mode, respectively. By weak indentation, the force in the range of 100 nN to 200 nN was applied to the sample surface. All samples were examined in a sealed chamber under ambient laboratory conditions (temperature: 24.5 °C, and relative humidity: $\sim 65\%$). In SKFM measurement, the scan rate is 1.82 Hz, the nap delta height is 50.00 nm, and the drive frequency is 70.668

kHz. The FE Simulation of the vertical piezoelectricity and sub-atom deformation actuator were conducted using a finite elements modelling software (COMSOL Multiphysic 5.0). Details can be found in the Supplementary Information.

6.3 Results and Discussion

6.3.1 Growth of CdS Thin Films

In this work, the CdS thin films were synthesized onto SiO₂/Si substrate by chemical vapor deposition (CVD) with sulfur powder and Cd grains as precursors. **Figure 6.3** shows three dominant morphologies of CdS thin film: i) uniform disc-like structures, ii) Janus- structure with two kinds of thickness at one thin film, and iii) rounded micro-particle on the center of thin film. The typical optical microscopic images are shown in Figure 6.3a, d and g, and all the samples are circular. The radius of as-prepared thin film is between 10 μm and 20 μm . In order to identify the thickness of as-prepared CdS thin films, the samples were characterized by atomic force microscopy (Figure 6.3b, c, e, and h). It is shown that the thickness of these thin films ranges from 2.1 to 3.7 nm, which is close to the thickness of 3 - 5 crystal lattices (2.02 nm for 3 lattices and 3.37 nm for 5 lattices) of hexagonal CdS along z orientation. The Janus-structure has different geometries at the thin film (Figure 6.3f). For the third structure, the circular micro-particles were grown on the thin film (2.2 nm). The height and radius of the particles are $\sim 1.4 \mu\text{m}$ and $\sim 5 \mu\text{m}$, respectively (Figure 6.3i). More than 100 CdS thin films were examined in order to calculate their size distribution (**Figure 6.4**). The three types of thin films present the average size of 8.92, 48.33, and 27.08 μm , respectively, with the Gaussian-distribution. The standard deviations of the size are 0.84, 17.65, and 7.75 μm , respectively. The average size of the Janus-structure is larger than that of the uniform disc-like structures, which suggests that the secondary nucleation could be preferentially formed in a large thin film.

Figure 6.3 CdS thin films with three different shapes. Typical optical images (a, d, g), and AFM images (b, c, e, h) of CdS thin films with uniform disc-like structure, Janus-structure, and the structure of rounded micro-particle on its center. The AFM line scan in c indicating the thickness of CdS ultra-thin film is ~ 3.2 nm, corresponding to ~ 5 lattices of CdS. The AFM line scans in (e) and (h) representing that the Janus-structure has two kinds of thickness (2.1 nm and 3.7 nm) at one thin film, and the structure of microparticle is grown on the thin film with the height of ~ 1.4 μm and radius of ~ 5 μm . Corresponding structural diagram shows in f, i.

Figure 6.4 Statistical analysis for the size of CdS thin films. Histograms of CdS size distribution with the morphology of (a) uniform disc-like structures, (b) Janus-structures, and (c) centre particle structures. The table summarized their average size and standard deviations, based on optical images including at least 100 flakes for each morphology.

6.3.2 Spectroscopic Characterization of CdS Thin Films

Raman spectra were collected from these materials. The wurtzite CdS can be identified by the Raman vibration modes [11,12]. The first-order longitudinal optical (1LO) and second-order longitudinal optical (2LO) phonons in CdS thin films were clearly observed from Raman spectra (**Figure 6.5**), which matched well with the Raman spectra of nanowires [12-14]. It is well known that the optical properties of nanomaterials show significant departures from their bulk counterparts, because the scale of confinement approaches their exciton Bohr Radius [15]. Notably, the thickness of our CdS thin films is in the range of 2 to 3 nm, which is closed to the exciton Bohr Radius of CdS (~3.1 nm) [16,17]. To understand the optical properties of as-prepared CdS thin film, their band gap structure and photoluminescence (PL) were investigated. **Figure 6.6a** represents the energy band structure of CdS in the vicinity of the Γ -point of the Brillouin zone, showing the direct-gap emission at Γ -valley (green arrow) as well as electron transitions between defect energy level and electron band (yellow arrow), which results in photo emission with band gap fluorescence and defect-related luminescence [7]. The PL properties for all three kinds of

CdS thin film were obtained at room temperature using 457 nm laser as an excitation source (Figure 6.6b-f, **Figure 6.7**). Only a strong emission peak at ~ 506 nm was observed from ultrathin CdS thin film with the thickness of 2-3 nm, which is considered to be band-edge emission.

Figure 6.5 Raman spectra of as-obtained CdS sample. (a) Raman signals from the centered particle, (b) thick film, (c) and thin film, showing the characteristic Raman peaks of CdS. The peaks at 302 cm^{-1} and 603 cm^{-1} correspond to the first-order (1-LO) and second-order (2-LO) longitudinal optical phonon bands of CdS, respectively.

Figure 6.6 Spectroscopic characterization of CdS thin film. (a) The energy band structure in the vicinity of the Γ -point of the Brillouin zone, showing the photon emission process. (b) Photoluminescence spectrum of CdS thin film from the point i and point ii marked in c with cross, showing strong band-edge emission (506 nm) of CdS ultra-thin film and defect-related emission (595 nm). (c) Optical image of CdS thin film with rounded micro-particle on its center. (d, e) PL mapping at the emission of 514 nm with different scale bar, demonstrating a high uniformity and homogeneity of CdS thin films at the outside area. (f) PL mapping at the emission of 595 nm, indicating the defect-related emission only occurs at the thicker CdS microparticle.

Figure 6.7 PL spectra and PL mapping from the CdS thin films. (a, e) Optical microscopic images of centered particle thin film and Janus-structure (two kinds of thickness at one thin film). (b, c, d) Corresponding PL mappings at the peak of 514 nm and 595 nm. (b and c show 514 nm mapping with different scale bars). (f) The PL mapping of CdS Janus-structure at the peak of 514 nm. (g) FWHM PL mapping at the peak of 514 nm. (h) PL spectra from the point A and point B in e, insert showing the strong PL emission from the point A and B.

Notably, the value is close to the band-edge emission of bulk CdS (~514 nm) with slight blue shift. Similar near-band-edge emissions from CdS quantum dots, nanowires, and nanoribbons were also observed in previous reports [7,18,19]. This phenomenon can be explained by quantum confinement effect in two-dimensional thin film. As the dimension of the materials reaches to nanoscale (close to the exciton Bohr Radius), the electrons and holes will be squeezed into a confining dimension, following the appearance of discrete energy states. Therefore, the band gap increases and becomes size dependent, which ultimately gives rise to a blue shift in band-edge emission [15,20]. For circular micro-particle on the center of the thin film, the PL spectrum displays pronounced peak at 595 nm other than band-edge emission at 514 nm (Figure 6.6), which is contributed to the

defect-related emission from trap or surface states, e.g. the unreacted sulfur atoms at the interface and Cd vacancies.

The PL spectra and PL mapping were collected from different types of CdS thin films (Figure 6.3d, e, f, **Figure 6.7**). Figure 6.6c shows the typical optical microscopic image of the rounded micro-particles on the center of thin film, and the corresponding PL intensity mapping at the peak of 514 nm. Different scale bars have applied to Figure 6.6d and e to reflect the fine structure of the CdS thin films. The PL mapping at the outside area suggests a high uniformity and homogeneity of CdS thin films. Meanwhile, the strong and ring-like PL emission was observed at the middle range of sample. The intensity of PL emission from micro-particle is extremely strong than that from thin film. Therefore, it is difficult to recognize the small distinction of PL mappings between those two materials, despite there is ~8 nm disparity for band-edge emissions at different positions. The intensity of PL mapping at 595 nm confirms that the defect-related emission only existed at the relatively thicker CdS rounded micro-particle. Those ring-like and size-dependent band-edge emissions, as well as strong defect-related emission, provide new possibilities for construction of optoelectronic devices.

6.3.3 Surface Potential and Vertical Piezoelectricity of CdS Thin Films

In order to investigate the surface potential of CdS thin films, the scanning kelvin force microscopy (SKFM) was carried out by non-contact probe scan mode. As shown in **Figure 6.8a**, SKFM can be used to explore the surface potential by tracking the electrostatic interactions between the tip and the sample surface. Such surface potential is related to the work functions of scanned materials, and reflects the local charge distribution when a bias voltage was applied to their surface. SKFM has been employed to measure the surface potential difference in 2D graphene-boron nitride heterostructures, as well as the doping and charge carrier concentration in semiconducting nanomaterials [21,22]. Figure 6.8c shows the band diagram change of AFM tip and sample in SKFM mode. The work function differences between the sample (ϕ_{sample}) and the probe (ϕ_{tip}) create a contact potential difference when they are electrically contacted. Therefore, tracking the contact potential

difference by applied the equivalent external voltage can determine the work function and local charge distribution at the surface of scanned samples. The SKFM mode was applied to the single CdS thin films with different tip voltages (3 V, 6 V, and 9 V). As seen from the topography and phase images shown in Figure 6.8e and f, the CdS thin film presents strong dark and light contrast than the substrate. Its thickness is ~ 3.09 nm and phase variation ~ 3 degrees. Figure 6.8g-i show the surface potential images with increased tip voltages, which indicate that the CdS thin film has higher positive voltage than the substrate. The surface potential of CdS sample can be quantitatively determined to be ~ 0.9 V higher than that of the substrate, indicating that a large amount of charges are accumulated at CdS thin film. I believe this was resulted from the piezoelectricity of CdS sample because the contact PFM was conducted several times before the non-contact SKFM measurement. Similar behaviors were also recorded from other CdS samples via SKFM. Before the CdS thin film was scanned by PFM tip, it showed ~ 200 mV surface potential higher than the substrate. After scanning, this value increased up to ~ 1 V (**Figure 6.9**). Such phenomenon indicates that the contact PFM process can largely change the surface potential of CdS thin film by producing the charges at its surface and the vertical piezoelectricity of CdS is the key to the generated charges.

Standard contact PFM technology was employed to investigate the vertical piezoelectricity of single CdS thin film. As shown in Figure 6.8b, the mechanical response of the sample was measured when applied the vertical electrical field to its surface through conducting PFM tip. It is known that a typical piezoelectric material will be strained (or stressed) under a vertical electrical field, which will be reflected in the amplitude change for PFM imaging. The vertical motion of PFM tip and the vertical electric field applied make the PFM imaging a powerful tool to explore the electromechanical functionalities in vertical direction, namely, quantify the piezoelectric constant of d_{33} for piezoelectric materials. Up to now, this technology has been extensively used to study piezo-/ferro-electric ceramic films and ZnO nanomaterials, such as nanowires and nanorods [23-28], as well as to image domain structures and domain evolution in ferroelectric thin films [29-32].

Figure 6.8 Non-contact SKFM and standard contact PFM investigation for CdS thin film. Schematic illustration of SKFM (a) and PFM (b) measurement. (c) Band diagram of tip and sample when they are electrically separated (top graph) and electrically contacted (bottom graph). (d) Optical image of CdS thin films. Topography (e) and phase (f) images observed by SKFM mode for the single CdS thin film marked in d. (g-i) Corresponding potential mappings with the tip voltages of 3V, 6V, and 9V, respectively. Insets show histograms of the surface potential distributions. The CdS ultra-thin film has ~0.9 V higher

positive voltage than the substrate, demonstrating that a large amount of charges are accumulated at CdS thin film after contact PFM scanning. (j) Amplitude images observed by contact PFM technology with the tip voltages from 1v to 6v, showing remarkable inverse piezoelectricity. (k) Average amplitude variations versus applied voltages calculated from j. The error bars indicate one standard deviation. The scale bar in e-j is 2 μm . The linearly fitted line shows that the measured piezoelectric coefficient d_{eff} is $\sim 16.4 \text{ pm} \cdot \text{V}^{-1}$, while the vertical piezoelectric coefficient d_{33} is $\sim 32.8 \text{ pm} \cdot \text{V}^{-1}$.

Figure 6.9 SKFM characterization of CdS thin film. (a, b, c, d) Topography, phase, amplitude, and potential of CdS thin film before contact PFM process. (e) Surface potential profile measured along dashed line in D (width: 30). (f, g, h, i) Topography, phase, amplitude, and potential of CdS thin film that after contact PFM process. (j) Surface potential profile measured along dashed line in i (width: 30). The change of surface potential after PFM scanning indicates that the contact PFM process could produce the charges at the surface of CdS ultra-thin film.

Here, PFM imaging was first employed for local characterization of ultra-thin CdS thin films. Tip voltages from 1 V to 6 V were applied to study the vertical electromechanical response of CdS thin films. The amplitude images under different tip voltages are shown in Figure 6.8j, and the corresponding topography and phase images are displayed in **Figure 6.10**. Surprisingly, significant amplitude change was observed in the amplitude images when applied different tip voltages, indicating the strong inverse piezoelectricity. The average amplitude variations can be calculated from the selected areas in Figure 6.8j (details in **Figure 6.11**). From average amplitude variations versus applied voltages in Figure 6.8k, the vertical piezoelectric constant of d_{eff} is measured $\sim 16.4 \text{ pm} \cdot \text{V}^{-1}$, which is not equal to the real vertical piezoelectric coefficient d_{33} because a non-uniform electric field is applied to the sample during the piezoelectric measurements. Pt/Ir-coated tip were used for PFM scanning, and the force applied is in the range of 100 nN to 200 nN. Such external force will result in a weak-indentation to sample, because the support of the rigid SiO_2 substrate. It is reported that AFM tip can only penetrate $\sim 3 \text{ nm}$ at SiO_2 [3]. The thin and soft nature of the CdS ($\sim 3 \text{ nm}$) makes sure the mechanical deformation of SiO_2 is the dominant contribution as shows in **Figure 6.12**. The stiff tip and surface, and high dielectric constant lead to a significant potential drop between the tip and surface, that is $V_s \ll V_{\text{tip}}$, and the contact area is negligible in this situation [34]. The nonplanar PFM tip and small deformation of rigid substrate results in weak indentation limit, which make the contact area with the sample less than the tip radius ($\sim 25 \text{ nm}$) (Figure 6.12). According to previous reports [32-34], the value of d_{33} is approximately twice than measured d_{eff} . Based on this, the piezoelectric coefficient d_{33} of the CdS thin film can be estimate to $32.8 \text{ pm} \cdot \text{V}^{-1}$, which is 3 times larger than that of the bulk CdS materials ($9.71 \text{ pm} \cdot \text{V}^{-1}$) and ZnO materials, even comparable to some of the inorganic piezoelectric ceramics (**Figure 6.13** and **Table 1**) [35]. Previous studies have demonstrated that the piezoelectric coefficient of CdS strongly depended on its carrier concentration. The d_{33} coefficient of CdS decreased by 60% when the carrier concentration increased from 10^9 to 10^{18} cm^{-3} [36,37].

Figure 6.10 Topography and phase images of PFM characterization of CdS thin film when applied different tip voltages (1-6 v). The topography images show that the CdS samples were not damaged when applying the external potential of 1-6 V on its surface. The phase images represent obvious phase variations of that from CdS ultra-thin film to substrate.

Figure 6.11 The average amplitude change can be established from 8 different areas of CdS sample. The average signals from the marked area of A_1 , A_2 , A_3 , and A_4 , indicate the average amplitudes on substrate at different locations. The average signals from the marked areas of AS_1 , AS_2 , AS_3 , and AS_4 , are the amplitude responses of CdS ultra-thin film at different locations. The variation of average amplitude from substrate to CdS sample represents the piezo-response of CdS ultra-thin film. For each sample, the total piezo-response and standard deviations were calculated from the average piezo-response at different location.

Figure 6.12 Illustration of weak-indentation and strong indentation. (a) SEM image of AFM Pt/Ir-coated tip with side-view; (b) geometry of the tip indenting the sample surface with weak-indentation and strong indentation.

Figure 6.13 Thickness vs. piezoelectric coefficient distribution from previous literature results. Our result presents the vertical piezoelectricity of final thin materials (~ 3 nm), and the piezoelectric coefficient d_{33} of CdS ultra-thin film is larger than that of most thin films (~ 100 nm), and 2 times larger than buck CdS.

Table 6.1 Summary of piezoelectric coefficients from different materials.

Materials	Piezo. Coefficient	Size	Reference
Bulk ZnO	$d_{33}=12.4$ pm/V	buck	<i>Ref. 40</i>
ZnO nanorods	$d_{33} = 0.4\text{--}9.5$ pm/V	150–500 nm	<i>Ref. 36</i>
	$d_{33} = 4.41 \pm 1.73$ pm/V		<i>Ref. 41</i>
ZnO nanobelts	14.3–26.7 pm/V	65 nm	<i>Ref. 42</i>
ZnO pillars	$d_{33} = 7.5$ pm/V		<i>Ref. 43</i>
NaNbO ₃ nanowires	0.85–4.26 pm/V	100 nm	<i>Ref. 44</i>
KnbO ₃ nanowires	7.9 pm/V	100 nm	<i>Ref. 45</i>
BaTiO ₃ nanowires	16.5 pm/V	120 nm	<i>Ref. 46</i>
GaN nanowires	$d_{33} = 12.8$ pm/V	64-191 nm	<i>Ref. 47</i>
PZT nanoshell	90 pm/V	90	<i>Ref. 48</i>
PZT nanowires	114 pm/V	75	<i>Ref. 49</i>
Phage based materials	7.8 pm/V	10-150 nm	<i>Ref. 32</i>
Buck CdS	$d_{33} = 9.71$ pm/V	Buck	<i>Ref. 50</i>
CdS thin films	$d_{33}=32.8$ pm/V	2-3 nm	This work

 (*Part of this table cited from **Ref. 35**)

In order to investigate the electrical conductivity of CdS materials, the Hall device and FET devices were fabricated (**Figure 6.14** and **Figure 6.15**). The Hall device presents poor conductivity, and here just pA level current can be detected under higher source-drain voltage, which makes it difficult working as Hall device for calculation of the carrier concentration. The field-effect transistor using the single CdS thin film was further fabricated (see Figure 6.15). The source/drain current was measured to be at pA level with a bias voltage (25 V) applied, indicating the low carrier concentration in CdS thin film. The carrier concentration (n_c) can be calculated by $n_c = 1/\rho e \mu_e$, where ρ is the resistivity, e is the electronic charge, and μ_e is the electron mobility [36]. The electron mobility (μ_e) can be estimated by $\mu_e = G_m(L/WC_g V_{ds})$, where G_m is the peak transconductance ($G = dI_{ds}/dV_g$), C_g is the gate capacitance, L and W is the channel length (7 μm) and width (10 μm), respectively. I deduce that the mobility μ_e is $0.0023 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and the carrier concentration n_c is in the range of $\sim 10^{12}$ to $\sim 10^{15} \text{ cm}^{-3}$. Therefore, this robust piezoelectric coefficient of CdS thin film is presumably due to the free boundary and low carrier concentration, which results from the low dimensional structure with large surface and defects.

Figure 6.14 Hall device of CdS thin film. (a) Optical image and (b) I-V curve of CdS Hall device. The Hall device presents poor conductivity, which makes it difficult working as Hall device for calculation of the carrier concentration.

Figure 6.15 Electrical characterization of CdS thin film. (a) Schematic illustration and optical image of FET device based on CdS thin film. (b) Transfer characteristic (I_{ds} - V_g curves) of a transistor. (c, d) Output characteristics (I_{ds} - V_{ds} curves) of device under dark and exposure by light, respectively. All data were measured at room temperature.

6.3.4 DART-PFM Technology for Imaging Vertical Piezoelectric Domain

The dual AC resonance tracking piezoelectric force microscopy (DART-PFM) was employed to understand the piezoelectricity of CdS thin films by in-site characterization. Although PFM technology is considered to be a powerful tool to monitor the electromechanical response of piezoelectric materials, it fails at rough surface or atomic thin films. For such samples, the noise floors of the surface height topography usually reach to tens of pico-meters (pm), which is comparable to the electromechanical displacement in atomically thin nanomaterials at the vertical direction. As shown in **Figure 3.6 of Chapter 3**, DART-PFM employs AC resonance tracking to measure the shift of resonance frequency, while avoiding crosstalk between changes in the contact resonance frequency and surface topography [38,39]. The DART-PFM has proven to be a reliable method to study the electromechanical elastic properties for inorganic ceramics and biological systems [38]. In this chapter, this technology was used to investigate the local piezoelectricity of the CdS thin films (**Figure 6.16a-k**). Figure 6.16a shows the height topography of single CdS thin film with the thickness of ~ 3.16 nm. The corresponding resonant frequency, phase, and amplitude images are displayed in Figure 6.16b-d. Interestingly, for the resonant frequency image, the CdS thin film (dark) shows a standing in remarkable contrast against the regions outside (bright) because the resonant frequency of tip-surface interaction changes from ~ 347 kHz to 342 kHz when the tip is applied to the CdS thin film. The corresponding phase change is also observed, as shown in Figure 6.16c. This variation of resonant frequency probably results from the tip-surface spring constant, which is originated from the electromechanical reaction and piezoelectric constant of the materials being scanned. In order to understand the vertical piezoelectric of the surface of CdS thin film locally, the imaging area was zoomed to $400\text{ nm} \times 400\text{ nm}$, as marked in Figure 6.16a. The top view of 3D topography, resonance frequency, phase, and amplitude images are shown in Figure 6.16e-h, respectively. The height topography represents that the CdS thin film is composed of the ultrathin nanosheets (the roughness is 0.67 nm). From marked areas in Figure 6.16f, the resonance frequency of small nanosheet varies from ~ 346 kHz to ~ 343 kHz at different locations. The contrast is clearly observed from the marked areas (I, II, III, IV, and V) in the overlap images of topography and frequency in Figure

6.16i, and the corresponding height profiles in Figure 6.16j and k. The dark areas represent low resonance frequency, implying the strong piezoelectric domains. Similar piezoelectric geometries were also found at the boundary between the CdS thin film and substrate, as shown in **Figure 6.17**. As mentioned above, the frequency response in such scanning model is dominated by the tip-sample electromechanical interaction, which mainly relies on the piezoelectricity and the crystallinity of samples. Therefore, it enables us to study the electromechanical properties locally on the rough surface of the atomic nanosheets.

Figure 6.16 DART-PFM technology for characterization of CdS thin film. Topography (a), resonance frequency (b), phase (c), and amplitude (d) images for single CdS thin film, and showing remarkable resonance frequency variations. Top view 3D topography (e), resonance frequency (f), phase (g), and amplitude (h) images for marked area in a. (i) The overlap image of topography and resonance frequency, marked areas present the notable

change of resonance frequency. (j, k) Height profiles measured by line scans along Line 1 and Line 2 in e, the shadow areas (I, III, and V) corresponding to marked areas in i.

Figure 6.17 DART-PFM characterization for the boundary of CdS thin film. Topography (a), resonance frequency (b), phase (c), and amplitude (d) images for the boundary of single CdS thin film, showing remarkable resonance frequency variations. (e) Histograms of resonance frequency from b, and displaying the ~3 kHz frequency change from the sample to substrate.

6.3.5 Simulation on Vertical Piezoelectricity and Actuator with Sub-atom Resolution

To better explain the experimental results of vertical piezoelectricity and estimate the deformation of CdS thin film under applied voltage, a 3D finite element (FE) model was developed with Comsol Multiphysics, as schematically shown in **Figure 6.18**. This model consists of a cone with half ball as the PFM tip with the diameter of 50 nm (Figure 6.18a), and one CdS sample with the thickness of 3 nm. In this simulation setup, the PFM tip contacts with CdS sample with 5 V DC voltage applied. The stress distributions on CdS sample were investigated, as shown in Figure 6.18c and d. It is found that the region surrounding the contacting point experiences the highest stress. The stress will then decay gradually towards edges of the CdS sample. The strong stress is contributed by the large deformation produced by vertical piezoelectricity of CdS sample. This unprecedented high vertical piezoelectricity ($d_{33}=32.8 \text{ pm}\cdot\text{V}^{-1}$) of CdS thin film allows extremely precise positioning at sub-atom level. 3D FE model was built to demonstrate this. The CdS thin film (thickness of 3 nm and radius of 15 nm) was employed as actuating material, and -1 to -5 V DC voltages were applied to its surface as driven voltage. Applying a negative tip bias to the CdS surface will lead to positive electrical field along vertical direction, and result in the expansion of materials. Figure 6.18e-g show the simulation results of strained CdS thin film with different voltage applied to its surface. By increasing the negative driven voltage from -1 V to -5 V, the deformation of CdS sample will be linearly increased from ~30 pm to ~150 pm (Figure 6.18e and f). This result is in accordance with experimental data. Although the roughness of CdS thin film is increased slightly under large potential (Figure 6.18e), the deformation magnitude remains linear dependency on the driven voltage at pm level, which is already close to the lattice constant of CdS. Our simulation demonstrates high vertical piezoelectricity in CdS quantum, which can be applied as active material for sub-atom deformation actuators.

Figure 6.18 Simulation of vertical piezoelectricity and sub-atom deformation actuator. (a) 3D image of potential drop on CdS film; (b) SEM image of conductive tip for PFM characterization; (c) and (d) bottom and side views of stress distribution on CdS film; (e-g) simulation for sub-atom deformation actuator; surface deformation curves (e) and mappings (g), and vertical deformation (f) of CdS thin film where applied different potentials.

6.3.6 Discussion of CdS Thin Films on Sensor Applications

Mechanical transducers have the inverse theory than actuators. Therefore, piezoelectric CdS thin film is also promising for sensor applications. Previous paragraphs have demonstrated that CdS thin films possess high d_{33} coefficient ($d_{33}=32.8 \text{ pm} \cdot \text{V}^{-1}$) of piezoelectricity. The value is 3 times larger than that of the bulk CdS materials ($9.71 \text{ pm} \cdot \text{V}^{-1}$) and ZnO materials, and comparable to most of the inorganic piezoelectric ceramics in

sub-70 nm scale. The CdS thin film has been demonstrated is capable as the driven material for actuators, and shows its resolution that can be reaches to sub-atom scale. Because pressure and strain sensors have inverse behavior than actuators, the giant piezoelectricity and high-resolution applications in actuators make the CdS thin film can be used in construction of high-sensitive pressure and strain sensors. The AFM tip was applied the tiny force ($\sim$ nN level) to the surface of CdS materials. This small force could produce a weak-indentation to CdS sample, and as a result of generated charges in its surface. The carrier concentration and resistivity of CdS thin film will be changed. It is easily to anticipate that the low-detection limit of CdS thin films based mechanical sensor can reaches to $\sim$ nN level, which is comparable to the single cell migration force [51-52]. Therefore, the CdS thin films are great candidate in fabrication of ultra-sensitive pressure and strain sensors for detecting the tiny pressure ($\sim$ nN level) and deformations (sub-nano scale). This high sensitivity provides their potential applications in monitoring the migration of single cell or cyto-active detection.

6.4 Conclusions

In summary, ultra-thin CdS thin films have been synthesized, and been demonstrated their strong vertical piezoelectricity at atomic scale (3~5 space lattices), by using non-contact SKFM, contact PFM and DART-PFM. The locally vertical piezoelectricity of CdS thin films was resolved using DART-PFM and determined the vertical piezoelectric domains at the CdS thin films. Their vertical piezoelectric coefficient (d_{33}) was measured to be $\sim 32.8 \text{ pm} \cdot \text{V}^{-1}$, three time higher than CdS bulk. In addition, vertical piezoelectricity in CdS thin film and its applications in sub-atom deformation actuator were demonstrated by 3D FE models. The strong vertical piezoelectricity makes this material promising for construction of atomically thin piezoelectric devices.

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Chapter 7

Micro-manufacturing for Flexible Sensor Arrays

The technology on integration of flexible sensing electronics is very important for commercialization of health monitoring system. In this chapter, the non-standard (non-silicon technology) MEMS technology was developed in the fabrication of smart and integrated flexible sensing electronics on a various kind of flexible plastic substrates such as PET and PDMS. As an example, the integrated smart flexible sensor contains 3×3 pressure sensor arrays were fabricated for monitoring body related pressure and the body temperature. The strong Van der Waals' force between two smooth PDMS substrate provides the flexible device with good stability and reproducibility. The results will pave the way for the practical application of such flexible sensing devices in real-timely and simultaneously monitoring multiple physiological signals such as wrist pulse and body temperature.

7.1 Introduction

Currently, various materials and technologies were developed for fabrication of flexible sensing electronics [1-9]. However, only a few reports on highly integrated flexible sensor arrays [10-12], and most of the flexible healthcare sensors contain single sensing units, which makes it has large bulk and power consumption as well as strong noisy from the environment. These disadvantages as barriers for putting the flexible sensors towards practical applications and commercialization. As such, this chapter proposed micro-manufacturing technologies such as microelectromechanical systems (MEMS) technology for fabrication of modularized flexible sensor arrays. The technology is compatible to various flexible substrate including PDMS, PET, and PI substrate. The obstacles in manufacturing process such as thermal expansion of flexible substrate were discussed, and resolving method was proposed. Finally, the MEMS technology was employed to fabricate the modularized flexible sensor arrays, and investigated their performance in monitoring the wrist pulse and body temperature.

7.2 Experimental Methods

7.2.1 MEMS Process for Micro-structured Si Mould

The patterned PDMS films with pyramid structures can be fabricated by micro-structured Si mould with inverted pyramid. The photolithography, dry and wet etching process were employed for fabrication of micro-structured Si mould. At first, the typical photolithography process (spin coating: 4000 rpm for AZ5214E; pre-bake: 2 min at 105 °C; exposure: 3s at 405 nm UV light of $\sim 42\text{mW/cm}^2$; develop: 30s at diluted AZ developer with deionized water) was used to fabricate the patterned photoresist at Si/SiO₂ substrate. Then, the exposed SiO₂ region can be dry etched by PECVD process at 80 mTorr with RF power of 100 W. The SiO₂ etch rate is $\sim 62\text{ nm/min}$ when the condition includes the CF₄ of 50 sccm and O₂ of 20 sccm. The photoresist was removed by acetone at room temperature. The SiO₂ film was patterned by this PECVD process. After that, the patterned SiO₂ can plays as covering and protected layers in NaOH solution to fabricate invert pyramid

structures. The wet etching process carried out in 35% NaOH solution at 85 °C, where the temperature was controlled by oil-bath. The anisotropic etching of Si appears in NaOH solution due to the large difference of etch rates for different crystal plane. The etch rates follow the order as: (110)>(100)>(111). Therefore, the invert pyramid structure can be obtained at Si (100) substrate by square pattern, which pre-prepared by PECVD and photolithography. The morphology and depth of pyramid structure can be controlled by reaction time. In this experiment, the fine invert pyramid structure can be achieved when the wet etch process was sustained to 40 min.

Figure 7.1 Wet-etching process for fabrication of patterned Si substrate with invert pyramid structures.

7.2.2 Flexible-based MEMS Technology for Modularized Sensor Arrays

The flexible and modularized sensor array was constructed on the pyramid patterned PDMS substrate. The pyramid patterned PDMS substrate was fabricated by using the invert pyramid structured Si substrate as hard mould. The PDMS mixture (Dow Corning Sylgard 184; the weight ratio of base to cross-linker was 10:1, the details can be found elsewhere) was spin-coated to Si mould at ~600 rpm, and solidified at 50 °C for 24 h to form the solid transparency film. Then, the PDMS film peeled off from the Si mould, and the pyramid structure has been copied from the Si mould to the surface of PDMS film. The PDMS solidification temperature is the key parameter for keeping the small thermal expansion of

PDMS, and results in the pyramid structure with the same size as Si mould. The metal electrode such as Au/Ti and Cu/Ti was fabricated on PDMS (or PE) substrate by photolithography with e-beam deposition, where the PDMS (or PE) substrate should be pre-treated by Oxygen-plasma PECVD to make sure the surface is hydrophilic and adhesive with photoresist. The modularized sensor array integrated with the temperature sensor and pressure sensors. Each unit layer was assembled and aligned by mask aligner. The strong van der Waals force between the smooth surfaces of PDMS makes the device integration with strong adhesive and more stability. The detailed process and parameters can be find at the **Figure 7.3**, *Appendix Table S2*, *Table S3*, *Table S4*, *Table S5*, *Table S6*, and *Table S7*.

Figure 7.2 Schematic illustration of fabrication of modularized sensor arrays.

7.2.3 Assembly for Flexible Sensors

Assembly process is one of the crucial steps for fabrication of modularized flexible sensors. Here mask aligner (Karl Suss, MJB4) equipment was employed assist to achieve assembly. As shown in **Figure 7.3**, the top flexible electrodes array was set on the glass substrate, and put it onto the mask holder. The bottom flexible electrodes array was installed onto the lifting stage where it covered with the dust-free paper tightly. The dust-free paper separated the bottom flexible electrodes array from lifting stage, and makes it left easily from the stage. Alignment of top electrodes array and bottom electrodes array is like alignment of photolithography. In this process, firstly, make sure the “alignment gap” lever is at the upper position. Then the contact lever was slowly and gently turned to move the bottom electrode of lifting stage up and close to (but DON’T contact) the top electrode. Opening the microscope illumination and using the binoculars or the TV screen display to observe the “cross” markers on both of electrodes. The bottom electrode can be moved using x-axis, y-axis, and θ -axis knobs. At the same time, the focus of “cross” markers on top and bottom electrode at different position, and should be adjust repeatedly to make sure the markers overlapped each other. Finally, put the “alignment gap lever” back and lift the sample of stage slowly in contact with the top flexible electrodes. The top and bottom electrodes were attached tightly by the van der Waals’ force, to form the flexible sensor arrays.

Figure 7.3 Photographs of mask aligner used in device assembly. The bottom and top electrodes were set onto the lift stage (a) and mask holder (b) respectively.

7.3 Results and Discussion

7.3.1 Fabrication of Flexible Micro-patterned Electrode

By the photolithography process, various microelectrodes have been produced on all kinds of flexible substrates such as PDMS and PET. **Figure 7.4** shows the photography of microelectrodes on PET and PDMS. The samples are translucent and flexible, which are important component units for flexible sensing electronics. The technology can realize the minimum linear resolution of $\sim 10\ \mu\text{m}$ for PET substrate, and $\sim 50\ \mu\text{m}$ for PDMS substrate. The conducting materials including Au, Ag, Al, Cu, and carbon have been used as electrode materials for device configuration. However, most of those conducting materials are rigid, and have derived cracks upon strong bend. The derived cracks can be eliminated by increasing the thickness of conducting materials only for the small bending with radius of curvature ($>5\ \text{mm}$). The thicker photoresist (with longer exposure time) was required for liftoff of photolithography, compared with traditional parameter.

Figure 7.4 Micro-patterned electrode on flexible substrate.

7.3.2 Thermal Expansion Affects the Resolutions

The temperature in solidification of PDMS is a key parameter for fabrication the electrodes on flexible substrate. The high temperature could accelerate the solidification of PDMS, and brings the thermal expansion to PDMS solution. Therefore, when the temperature down to room temperature, there will produce the lateral strain on PDMS substrate (**Figure 7.5a**). After the patterned PDMS peeled off from Si mould, the lateral strain makes the patterned regions of PDMS substrate shrinking and moving. The distance between each pattern region of PDMS is smaller than that of the Si mould. Therefore, it is hardly aligned the second photolithography process to the pre-patterned pyramid structures. The higher solidification temperature leads the large lateral strain of PDMS. For example, the PDMS was solidified at 80° for preparation of pyramid structures, the second photolithography and e-beam deposition were used to fabricate patterned Cu electrodes. Figure 7.5b to d, show the microscopy images of patterned electrodes on PDMS substrate from the point I', II', and III' in a. If kept the electrode of I' point aligned well with the pre-patterned pyramid PDMS, the point II' and III' show large deviation and mismatch to the pyramid structures due to the large deformation of substrate. There are two ways for elimination of the deviation and mismatch. One way to design the new masker for electrode fabrication, where the electrode size and spacing were re-defined by considering the thermal expansion of PDMS. The second way is to eliminate the lateral strain by decrease the solidification temperature. In our experiment, when the solidification temperature decreased to 45°, the alignment can be easily carried out due to the small deformation of patterned PDMS substrate. The solidification process was prolonged to 24 hours. The electrode patterns were well constructed onto the pyramid structures, as displayed in Figure 7.5e to g. The uniform and smooth Cu electrode covers the whole region of pyramid structures, while the pyramid structure was not destroyed in this process (Figure 7.5h and i). The wrinkle structures of Cu electrode make the devices have good stretchability (Figure 7.5j). Therefore, low solidification temperature could bring small lateral strains to PDMS substrate, and improve the accuracy for followed micro-manufacturing of flexible electrode.

Figure 7.5 Thermal expansion of pyramid PDMS substrate. (a) Schematic illustration of the thermal expansion process; (b-d) Microscopy images of flexible pyramid PDMS substrate with Cu electrodes, where the thermal expansion brings the dislocation to the pressure units of I' II' and III'; (e-g) Microscopy images of flexible pyramid PDMS substrate with well aligned Cu electrodes; (h-j) High-magnification microscopy images from the well aligned Cu electrodes, indicating the pyramid structures were not destroyed in the followed process for Cu electrodes.

7.3.3 Suspending the Film on PDMS Substrate

Suspended structure play an important role in construction of mechanical sensors. Previous research also has demonstrated that the suspended structure is the main part of sensor chip [13-16]. For example, the suspended graphene can be used to improve the sensor signal and reduce noise in aqueous solutions [13]. The suspended bilayer graphene shown the capability in detection of individual CO₂ molecular at room temperature [15]. Suspended 3D spiral structures and 2D MoS₂ materials have been demonstrated in application of vibration sensor and pressure sensor respectively [14, 17]. Here developed an effective method to suspend the conducting film onto stretchable PDMS substrate. As an example, the Cu film can be suspended onto PDMS substrate. The patterned Cu film was fabricated by photolithography (**Figure 7.6a**). Then, the PDMS can be etched by PECVD with the mixture gases of CF₄ and O₂ at room temperature. The solid PDMS substrate was reacted with etching gases, and the produced vapor (SiF₄, CO₂ etc.,) dispersed and escaped through patterned metal film where the PDMS substrate was exposure to reaction gases. Finally, the Cu film can be suspended controllably and partly onto the PDMS substrate by adjusting the reaction time. This suspended structure is promising in applications of flexible mechanical sensors such as flexible acoustic sensor.

The size of suspended region can be readily controlled by changing the reaction times. Longer reaction time produced larger suspended area of Cu film. The etching process was controlled from 0 min to 120 min, and the samples were collected for studying the etching process. **Figure 7.7a-d** show the optical microscopy images of samples with the reaction time of 30 min, 60 min, 90 min, and 120 min, respectively. The images marked with i' are dark-field optical microscopy images, corresponding to the upper optical microscopy images, and indicate that the relative dark areas around black points are the suspended regions of Cu film. Obviously, the size of suspended region is linear increased with the reaction time (**Figure 7.7e**). The etching rate can reach to ~340 nm/min. The largest coverage rate of suspended Cu film is ~4, where I defined the coverage rate is the ratio of suspended Cu film to un-suspended film at the PDMS substrate.

Figure 7.6 (a) Schematic illustration of manufacture steps for suspended Cu film on PDMS substrate. (b) Optical microscopy image of suspended Cu film on PDMS substrate, where the black region is the hole, and the relative dark region is suspended area. (c) Optical microscopy image of patterned Cu film on PDMS substrate before etching, the black square points are the holes where the Cu film was removed and the PDMS was exposed. (d) Optical microscopy image of suspended Cu film on PDMS. (e) Dark-field optical microscopy image of the PDMS substrate after removing the Cu film by wet etching, which suggests the holes were fabricated under the Cu film.

Figure 7.7 (a-d) The optical microscopy images of samples with the reaction time of 30 min, 60 min, 90 min, and 120 min, respectively. The images marked with i' are dark-field optical microscopy images, corresponding to the upper optical microscopy images. These optical microscopy images indicate that the relative dark areas around center black points are the suspended regions of Cu film, and increased with the reaction time. (e) The graph of the etching length with reaction times, suggests the suspended regions are linear increased with the reaction time. The etching rate can be reaches to ~340 nm/min.

7.3.4 Integrated Flexible Healthcare Sensor Arrays

As an example, the modularized smart flexible sensor arrays were fabricated by micro-manufacturing process. As illustrated in **Figure 7.8a**, the modularized flexible health sensor comprises piezo-resistive pressure sensor arrays and temperature sensor. The pressure sensor arrays contains 3×3 units for monitoring the body related pressure signals such as wrist pulse. The temperature sensor was used for tracking the body temperature. The pressure sensor array was fabricated by the Cu electrode on the patterned PDMS substrate, where the pyramid microstructures for enhancing the sensitivity of pressure sensor. The whole device was manufactured by photolithography process, aligned by mask aligner, and integrated layer by layer to form the flexible health sensor. The device is flexible, translucent, and stretchable to some extent (Figure 7.8b). The pyramid microstructured PDMS substrate is the crucial part of device. Typically, the Si substrate of inverse pyramid structures was used as template for fabrication of pyramid patterned PDMS (Figure 7.8c). The Si substrate was patterned by the photolithography, and processed with dry etching and wet etching, the inverse pyramid structure was fabricated on the Si substrate due to the anisotropic etching of Si at 35% NaOH solution. The PDMS solution was spin coated to the Si mould and solidified. The pyramid patterned PDMS film can be obtained by peeling off it from the Si mould. Figure 7.8d shows the SEM image of the pyramid structures of PDMS film, indicates the inversed structure and the same size was successfully reproduced from the Si mould. The patterned Cu/Ti electrodes on pyramid structured PDMS substrate were fabricated by photolithography and e-beam deposition. Then, the PDMS substrate of Cu/Ti electrodes were face to face sticking, where each unit should be enable the top electrode is aligned well with the bottom electrode, and to form the piezo-resistance pressure sensor arrays. The configuration of each unit for pressure sensor as illustrated in Figure 7.8e, the sensitive contact sites at the top of pyramid structures make the device possess high sensitivity for the tiny pressure. When the pressure applied to the device, the deformation occurred at the top of pyramid structure, which could bring the modification for the contact sites and results in the resistance change of device.

Figure 7.8 Modularized flexible sensing device. (a) Schematic illustration of hybrid flexible sensing device, which contains the temperature sensitive part and the 3×3 pressure sensor arrays; (b) The photography of modularized flexible pressure sensors; (c) SEM image of inverse-pyramid structured Si mould; (d) SEM image of as-prepared pyramid structured PDMS substrate; (e) The illustration for the configuration of pressure sensitive unit.

The van der Waals reaction is different from chemical force like covalent bonds and ionic bonds, it is related the residual attractive or repulsive force between molecules. Current research has demonstrated that van der Waals force is strong in some practice applications such as Geckos can easily stick to walls and ceilings. Inspired by this, the strong van der Waals force at the interface of two smooth PDMS films was used for enhancing the stability and reproducibility of flexible sensor devices. The van der Waals force enabled each part of device stick together tightly and stably. **Figure 7.9a** shows the microscopy images of flexible device and elements. The pressure sensitive unit was constructed with the pyramid

patterned top electrode and smooth bottom electrode (right side in a). When the top electrode and bottom electrode were overlapped by face-to-face, the outside areas of pyramid structures can be tightly stuck by the strong van der Waals force from the smooth PDMS films (Figure 7.9b). The pyramid structure and its height difference brings the air cells to the interface between top electrode and bottom electrode, as marked in Figure 7.9a. These air cells make the device with high sensitivity for the tiny pressure. According to the previous reports, the wavy ribbons and wrinkles can make the device present stretchable and flexible. Figure 7.9c shows the zigzag wrinkled structures of Cu electrode, which can be realized by controllable stretching and folding of the manufacturing process.

Figure 7.9 The strong van der Waals force enable the flexible device tightly stuck. (a) Microscopy of the pressure sensitive unit as well as the elements of the top electrode and bottom electrode; (b) Illustration on strong van der Waal force exists at the interface of two smooth PDMS substrate; (c) Microscopy images of Cu electrodes show the zigzag wrinkled structures of Cu electrodes.

The modularized smart flexible sensor array can be attached to human body for tracking the health-related physiological signals. Traditional Chinese medicine propounded that persons' health condition can be evaluated by the body wrist pulse, and the diseases can be diagnosed from the different types of wrist pulse contours [18,19]. Modern medicine also demonstrated that wrist pulse is one of the most important physiological signals for human body, reflecting the blood pressure, heart rate, and the cardiovascular disease like atherosclerosis. The standard wrist pulse contains percussion wave (P-wave), tidal wave (T-wave), Valley and diastolic wave (D-wave), which caused by clinical information such as the systolic and diastolic blood pressures, as well as the ventricular pressure and the heart rate [20-22]. Currently, numerous flexible pressure and strain sensors were developed to do it, and various type of wrist pulse were obtained (**Figure 7.10**) [4, 5, 23-29]. Typically, the standard wrist pulse can only be obtained at the specific position of wrist. Multiple tentative tests were required for getting the accurate wrist pulse, which is time-consuming and hardly to do for the person of infirm body. To resolve this issue, the 9 sensing units (#1 to #9) were designed for monitoring the wrist pulse (Figure 7.8a, b, and **Figure 7.11b**). The sensor array has larger sensing region than single sensor. The prepared flexible sensor array (including 3×3 units) was attached to wrist for monitoring the wrist pulse, as shows in Figure 7.11a. For our sensor array, 3 out of 9 sensing units (#1, #6, #9) are electrical broken due to the defective manufacture, original from the mismatch of mechanical properties between patterned Cu film and PDMS substrate. Figure 7.11d show the normalized real-time I-t curves collected from the sensing units of #2, #3, #4, #5, #7, #8, suggesting #2 and #3 capable in recording the standard wrist pulses while other sensing units have difference pulse contours.

Figure 7.10 Various wrist pulse with different contours, the curve in *a* shows the standard wrist pulse.

Figure 7.11 Modularized flexible sensor array for monitoring the wrist pulse. (a, b) The flexible sensor array including 9 sensing units (#1 to #9), and was attached to human wrist. (c) The standard human wrist pulse can be obtained by the modularized sensor array. (d) Real-time I-t curves of the sensing units (#2, #3, #4, #5, #7, and #8) in monitoring the wrist pulse.

Body temperature is one of the important characters to evaluate the body conditions. To real-timely detect the temperature change, the modularized flexible sensor array was integrated with temperature sensor. 3D graphene with diluted PDMS was employed as temperature sensing materials (**Figure 7.12a** and b) because PDMS is sensitive to temperature and will expanded when temperature increased. In the composite of 3D graphene and PDMS, the graphene is play as a conductor where the charges and electrons can be through it. The PDMS is the insulator. As shows in Figure 7.12a, high temperature (T2) give rise to the expanded PDMS, and strained to the graphene, finally leads the conductivity change of graphene. Figure 7.12 c and d show the real-time I-t curves of the temperature sensor on temperatures in the range of 25 °C to 50 °C and 34 °C to 42 °C respectively. The results indict the sensor is sensitive in body temperature range. However, the high noisy makes our sensor is hard to distinguish the temperature to 0.1°C level. The sensitivity need further improved for clinical applications.

Figure 7.12 3D graphene/PDMS based temperature sensor unit in modularized flexible sensor arrays. (a) Schematic illustration of temperature sensing theory of 3D graphene/PDMS. (b) Microscopy image of 3D graphene with diluted PDMS. (c, d) Normalized real-time I-t curves of temperature sensor under the temperatures in the range of 25 °C to 50 °C and 34 °C to 42 °C respectively.

7.4 Conclusions

In this chapter, micro-manufacturing technologies such as MEMS technology were developed for modularized and integrated flexible sensing electronics. As an example, the modularized flexible sensor arrays were fabricated by MEMS technology. The modularized flexible sensor array contains 9 pressure sensing units and a temperature sensing unit, and presents reliable performance in monitoring the wrist pulse and body temperatures. It can be employed for tracking physiological signals for healthcare. The experimental parameters of micro-manufacturing technology can be referred to fabricate minimized flexible sensor arrays for the future research.

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Chapter 8

Conclusions and Recommendations for Future Works

In this chapter, the main findings and outcomes of the thesis are briefly summarized. Three different types of nanomaterials, including programmable high crystallinity carbon patterns, self-crosslinked carbon nanorod arrays, and CdS ultrathin films were developed for flexible sensing electronics, and be demonstrated the unprecedented good performance in flexible health-related sensors. The thesis also established the micro-manufacturing technology for fabrication of modularized and integrated flexible sensor arrays. These main outcomes and findings are significant to design the next generation of flexible health-related sensors. The recommendations for future works have also been proposed by material view and technology view.

8.1 Conclusions

By this PhD project, three novel nanomaterials were developed to meet the required materials of next generation flexible sensing electronics. They are: programmable carbon patterns, self-crosslinked carbon arrays, and ultra-thin CdS films. The growth mechanism and applications in construction of flexible sensing electronics were fully investigated. The micro-manufacturing technologies in fabrication of modularized flexible sensing electronics and integrated flexible healthcare sensor arrays were established. The technology minimized flexible sensors, and brings them towards smaller, smart, and less power consumption. The specific conclusions are summarized as follows:

- (1) High crystallinity carbon pattern was developed, which is different with graphene but remains the high crystallinity of sp^2 structure. Inspired by PPF and the conventional photolithography process, an effective method was proposed for synthesis of high-quality micro-patterned carbon by pre-patterning pyrolyzed photoresist as the solid carbon precursors. This precursor can produce high crystallinity carbon patterns with a high lateral resolution of $\sim 2\ \mu\text{m}$, which approaches the limit resolution of the traditional near-UV photolithography at hard contact mode and meets the requirement of the most flexible electronics. Bendable electronic devices have been fabricated based on the high-quality micro-patterned carbon. The bendable graphene device can stand the bending angle from 0° to 180° and present distinct output response for tensile and compressive strain with high sensitivity, which makes it promise in the construction of flexible mechanical sensors. These results will pave the way to next-generation carbon-based mechanical sensors.
- (2) 3D self-crosslinked carbon arrays were synthesized in the first time, and their applications in flexible sensing electronics for the detection of Parkinsonian tremor were demonstrated subsequently. The self-crosslinked carbon array is composed of a new type of carbon materials which is an “intermediate” form between the carbon nanotube and carbon nanofiber. The self-crosslinked structure enhances the contact points between individual carbon units and eradicates the electrical instability by reducing the residual stresses in the material. The CA-based flexible sensors show high

- sensitivity and good stability ($\sim 10,000$ times) in the detection of flexions and low frequency vibrations (< 6 Hz), and are capable in monitoring the Parkinsonian tremor.
- (3) Ultra-thin CdS films were synthesized, and vertical piezoelectricity in atomic scale (3~5 space lattices) has been demonstrated firstly. By employing complementary technologies such as in-situ scanning kelvin force microscopy, single and dual-frequency resonance tracking piezoelectric force microscopy, the locally vertical piezoelectricity and the vertical piezoelectric domains at the CdS thin film were determined firstly. Their vertical piezoelectric coefficient (d_{33}) was measured to be $\sim 32.8 \text{ pm} \cdot \text{V}^{-1}$. This value is higher than most of traditional piezoelectric materials. These findings will shed light on the design of new type of sensors and micro-electromechanical devices, and especially, the new generation of actuators with a sub-atom resolution.
- (4) The non-standard micro-manufacturing technologies for fabrication of modularized flexible sensing electronics were established. The technologies are compatible to various flexible substrate such as PET and PDMS. The modularized and integrated flexible sensor array was demonstrated by micro-manufacturing technology, and shows unpredicted performance in monitoring multiple health related physiological signals such as wrist pulse and body temperature. These results and experiment parameters can be broadened to fabricate the high integrated flexible healthcare sensors.

8.2 Future Works

8.2.1 Material View: Atomic layered materials for Flexible Healthcare Sensors

Atomic-thin (or monolayer) 2D materials are promising for flexible electronics. By structure engineering of materials, the thinner material suffered smaller strain when it was applied with a bend. It is because the thickness of material increased strain for the outmost side of materials upon bending. For example, the single-layer paper is easy to be bend than the multiple-layer papers (**Figure 8.1a**).

Figure 8.1 (a) Single-layer paper and multiple-layer papers on bend, indicates the single-layer paper is easier to bend than multiple-layer papers. (b) Atomic landscape of 2D Materials. Left-Top: Metal chalcogenide layers. Left-Bottom: Metal dichalcogenide layers. Metal could be W, W, Ti, Pt, Pd, Sn, Fe et al and chalcogen could be S, Se and Te.

Previously, the most widely studied 2D nanomaterial is graphene because of its versatile physics and high mobility [1, 2, 3]. However, the zero-band gap of pristine graphene limited its many applications such as used in transistor and sensor as channel materials, the transistor has low on/off ratios and cannot be switched off effectively. In contrast to graphene, 2D transition metal dichalcogenides (TMDs) will provide more opportunities because the electronic structures of TMDs could be readily tuned by their structures, size, and composition [4, 5]. Typically, TMDs have a common structural formula MX_2 , where M stands for transition metals (Mo, W, Ti, etc.) and X for chalcogens (S, Se, Te). The structure of TMDs is shown in Figure 8.1b. Each layer typically has a thickness of $6\sim 7 \text{ \AA}$, which consists of a hexagonally packed layer of metal atoms sandwiched between two layers of chalcogen atoms. The intra-layer M–X bonds are predominantly covalent in nature. For instance, the bandgap of MoS_2 could change from the bulk indirect of 1.3 eV to a direct bandgap of 1.8 eV in single layers [6]; the edge termination with different atoms

provide versatile surface chemistry properties, also the quantum size effects induce shifts in the valence band and the oxidation potentials [11]. Therefore, 2D TMDs provide the new avenues for flexible electronics by their remarkable chemical, mechanical, thermal, and electronic properties.

Recently, various and exciting 2D ultrathin layers such as Graphene, h-BN, MoS₂, MoSe₂, WS₂, WTe₂, ReS₂, PbI₂, InSe and In₂Se₃ can be synthesized by CVD method. These novel materials also shown the exciting applications [7-21]. It is noted here the largest single-crystal MoS₂ can be make up to mm size on Si/SiO₂ wafer, perfectly for massive device fabrications. Based on these novel 2D nanomaterials, the next-generation portable personal health-monitoring system was proposed, which makes use of the flexible and wearable sensing electronics to address the human health conditions. And the health monitoring system provides a convenient way for pre-diagnosis and prevention of diseases. In addition, such continuous monitoring device offers a new opportunity to avoid misdiagnosis and missed diagnosis in clinical practice.

As summarized in *Chapter 2.1.2*, there are three different configurations of flexible sensing devices that have been proposed and demonstrated: (i) piezo-resistive sensor, (ii) capacitive sensor, and (iii) field-effect transistor (FET). The first FETs based flexible pressure sensor was reported and named with “electronic skin” in 2004. This device was constructed using organic semiconductor film as channel materials [22, 23]. Typically, the fabrication of a sensitive skin consisting thousands of pressure sensors, which would require a flexible switching matrix that cannot be realized with present silicon-based electronics [22]. Organic FETs can replace for such conventional process not only because their inherently flexible and potentially low cost for large area, but also the simple manufacture process for integration of large area, such as ink-jet printing technology and aerosol-jet printing technology. In the followed years, multifunctional features of FETs based sensors, such as combination of pressure and temperature sensor, pressure sensor and organic light-emitting diodes (OLED)/nanowire based LED, have been demonstrated using pentacene, Silicon nanowires, vertical ZnO nanowires, and carbon nanotubes as the semiconductor for FETs and diodes [24-27]. The multifunctional electronics represent a new route towards the

flexible consumer electronics by optical and mechanical means, with potential applications in human-machine interaction, touch screen, robotics, optical MEMS and medical/health monitoring system. However, the organic electronics require high working gate voltage that confines their applications in wearable/attachable electrical systems, also, toxicological properties of organic semiconductors limit their applications on intrusive medical examinations such as surgical gloves and cardiac ablation therapy. In general, FETs based flexible pressure/strain sensors tend to be more sensitive than resistive and capacitive sensing devices because of the capacity to tune the conductance of channel semiconducting materials by controlling the gate voltage. These features make FETs ideal candidates for flexible electronic sensing devices, although these types of devices are more complex in structure, manufacture process and supplementary electronics than resistive and capacitive one.

From the view of materials, metal chalcogenides, especially the narrow band gap layers of MoS_2 , WS_2 , MoSe_2 and WSe_2 [5, 28, 29], is an excellent layered material complementary to half-metallic graphene and insulating h-BN atomic layers. The first electrical measurements of monolayer MoS_2 (by mechanical exfoliation method) were reported by Novoselov et al in 2005 [29], in a back-gating transistor configuration with the mobility in the range of $0.2\text{-}1\text{cm}^2/\text{Vs}$. The mobility of MoS_2 atomic layers has been improved to above $100\text{ cm}^2/\text{Vs}$ recently.

Figure 8.2 Schematics of flexible sensing devices. (a) traditional back-gate FET devices; (b) typical configuration of FET-based flexible sensing devices; the top view illustration of (c) single unit and (d) matrix of our flexible sensing devices.

A typical 2D FET device is shown in **Figure 8.2a**. Therefore, the 2D TMDs should be the promising candidate for channel materials of FETs. The FET-based flexible sensing device and matrix in Figure 8.2b and c were proposed. Atomic 2D TMDs were employed as channel materials, the carbon-based nanomaterials such as graphene and CNTs can be used as sensing materials. Figure 8.2b illustrates a typical configuration of FET-based flexible sensing device. This is a three-terminal electronic device, and the current flowing between source and drain can be controlled by the gate voltage. The sensing materials were integrated into the gate for changing the gate voltage at different external stimulation, such as temperature and pressure. Due to high on/off ratio in TMD based FET, small change of the gate voltage under stimulation will largely influence the current from source to drain, and bring great contributions to the sensitivity of this type of sensing devices. The matrix device is a significant innovation for its application in monitoring physiological signals. It will provide high resolution and accurate location of signals from human body.

8.2.2 Technology View: 3D-printing Technology for Flexible Healthcare Sensors

The 3D printing technology could reduce the cost of flexible sensing devices by simplifying the manufacture process, and saving the time. When the different inks (e.g. substrate polymer ink, conducting ink, and active semiconducting ink) were prepared, and the prototypes of devices were designed in computer, the fabrication of flexible devices can be achieved in more effective way. The large-scale fabrication can be achieved by printing multiple devices simultaneously, rather than the traditional step-by-step and one-by-one manufacturing technology. For the new products and designs, the 3D printing technology just needs to make the change of designs in computer, without facility change into the production line. The other cost reduction from the low operation and maintenance fees in this 3D printing process. It only needs to keep the small area of core printing nozzle and sample in dust-free environment instead of the large area clean room. The traditional MEMS technology required the manufacturing process at clean room, which is expensive to run.

3D printing technology can bring various functional materials to manufacturing process, and enhances their performance in monitoring physiological signals. For example, various versatile active materials, including conducting polymers, CNTs, reduced graphene oxide, 2-dimensional TMD flakes, can be prepared in the form of printing inks. Due to their unique physical and chemical properties, such as good conductivity, high mobility and on/off ratio, good thermal and mechanical stable, tunable bandgap, as the building blocks in flexible electronics, these nanomaterials could reduce the power consumption, save the battery life, eventually prolong the working duration. Furthermore, these novel functional nanomaterials put the flexible sensing devices with multi-functionality, ultra-sensitivity, high stability and reproducibility. And the capability of non-intrusive monitoring human physiological signals such as heart rate, wrist pulse, muscle movement, and pressure from sole of foot. 3D printing technology could easily to realize the arbitrary combination of such nanomaterials in the fabrication of flexible sensing devices. Therefore, the proposed 3D printing technology in construction of flexible electronics will endowed the device with new functionality and good performance in detection of human physiological signals for wearable healthcare.

3D printing for micro-structured electrodes and active materials. It is well-known that inorganic semiconductor materials are brittle and typically fracture under a strain of $\sim 1\%$, which poses a challenge to incorporate them into stretchable devices. Besides increasing the intrinsic stretchability of the building blocks such as organic molecules, stretchable architectures was effective way to realize mechanical stretchability for inorganic materials. Mechanical buckling has been exploited to enhance the stretchability of silicon (Si) nanoribbons by making them into wavy shape. The “S” shape of Au electrode represents stable output when stretched with large deformation. These special structures can be reversibly stretched and compressed to large extent without fracture, which is like the motion of a spring. Recently, “S” shape of graphene ribbon (catalytic synthesized by Cu wires) has been demonstrated the stable electrical performance (**Figure 8.3**). For improving the stability of flexible devices, 3D printing technology to construct electrode materials with “wavy” shape and “S” shape is the good candidate.

In general, the 3D printing technology could largely reduce the fabricating cost, and enable the large-scale and mass customization of electronic sensing devices, which improve the comfortability, convenience, and security of health-monitoring in clinical diagnoses and daily life.

Figure 8.3 3D printing technology to construct flexible electrode with “wavy” and “S” shapes.

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Appendix

The appendix contains the summary of chemicals and some important parameters for micro-manufacturing of flexible devices.

Table S1 Summary of Chemicals used in the thesis

No	Reagent	Purity	Company
1	Sulfur	99.98%	Sigma-Aldrich
2	Cadmium	99%	Sigma-Aldrich
3	Iron(III) chloride hexahydrate	97%	Sigma-Aldrich
4	Poly (pyromellitic dianhydride-co-4,4'-oxydianiline)	80% NMP/20% xylene	Sigma-Aldrich
5	Copper wire	99.99%	Sigma-Aldrich
5	H ₂ gas	99.999%	Leeden National Oxygen
6	CH ₄ gas	99.999%	Leeden National Oxygen
7	Ar gas	99.999%	Leeden National Oxygen
8	Buffered Oxide Etch	7:1	MicroChemicals
9	Photoresist AZ 5214E	28.3%	MicroChemicals
10	AZ Developer		MicroChemicals
11	PMMA		MicroChemicals
12	Polydimethylsiloxane	Sylgard 184	Dow Corning
13	Nikel	99.95%	Zhongnuo AdvMater
14	Copper	99.99%	Zhongnuo AdvMater
15	Gold	99.99%	Zhongnuo AdvMater
16	Titanium	99.99%	Zhongnuo AdvMater
17	Chromium	99.99%	Zhongnuo AdvMater

Table S2 Alignment masker definition for negative-pattern mask on Si substrate.

Step No.	Step description	Parameters
1	Spin coating PR	AZ 5214E, 4000 rpm for Si substrate,
2	Bake	Hot plate, 105 °C, 2 min
3	Exposure	405 nm UV light, 42 mW/cm ² , Hard contact, 3 s
4	Development	AZ developer: H ₂ O=1:1, 20 s, DI water

Table S3 Typical etching experiments in this thesis.

Materials	Method	Solution/ Atmosphere	Reaction time (min)	Temperature	Template
SiO ₂	Wet etching	BOE	2-3 min for 290 nm	RT	PRAZ5214 (positive and negative)
SiO ₂	Dry etching (PECVD)	CF ₄ , O ₂	5-6 min for 290 nm	25°	PRAZ5214 (positive only)
Si	Wet etching	35% NaOH	45 min	85° (Oil bath)	290 nm SiO ₂
PDMS	Dry etching (PECVD)	CF ₄ , : O ₂ 60:20 sccm	4 h for 50 μm	25°	Metal (Cu)
PI	Dry etching (PECVD)	CF ₄ , : O ₂ 20:60 sccm	4 h for 50 μm	25°	Metal (Cu)
C	Dry etching (PECVD)	O ₂ plasma	15 min for 1 μm	25°	

Table S4 Alignment masker definition for negative-pattern mask on flexible substrate.

Step No.	Step description	Parameters
1	Pre-treatment	Oxygen-plasma (described at Table3.3)
2	Pre-bake	Hot plate, 105 °C, 1 min
3	Spin coating PR	AZ 5214E, 2000rpm for PET substrate, 1000rpm for PDMS substrate, 30 s
4	Bake	Hot plate, 105 °C, 2 min
5	Exposure	405 nm UV light, 42 mW/cm ² , Hard contact/Soft contact/gap, 4.5 s/5 s
6	Development	AZ developer: H ₂ O=1:1, 20-30 s, DI water

Table S5 Alignment masker definition on flexible substrate for positive-pattern mask.

Step No.	Step description	Parameters
1	Pre-treatment	Oxygen-plasma (described at Table 3.5)
2	Pre-bake	Hot plate, 105 °C, 1 min
3	Spin coating PR	AZ 5214E, 2000rpm for PET substrate, 1000rpm for PDMS substrate, 30 s
4	Bake	Hot plate, 105 °C, 2 min
5	Exposure	405 nm UV light, 42 mW/cm ² , Hard contact/Soft contact/gap, 4.5 s/5 s
6	Bake	Oven, 110 °C, 9 min
7	Flood exposure	405 nm UV light, 42 mW/cm ² , 25 s
8	Development	AZ developer: H ₂ O=1:1, 20-30 s, DI water

Table S6 PECVD definition for etching SiO₂ layer

Step No.	Step description	Parameters
1	Pump down	Pressure: 2 mTorr, Time: 1 min, RT
2	High vac turbo pump	Pressure: 1.0×10^{-11} , Time: 3 min, RT
3	Gas stabilization I	80 mTorr, CF ₄ : 50 sccm, O ₂ : 50 sccm, Time: 30 s, Temperature: RT
4	Gas stabilization II	80 mTorr, CF ₄ : 50 sccm, O ₂ : 35 sccm, Time: 30 s, Temperature: RT
5	Gas stabilization III	80 mTorr, CF ₄ : 50 sccm, O ₂ : 20 sccm, Time: 30 s, Temperature: RT
6	Etching process	80 mTorr, CF ₄ : 50 sccm, O ₂ : 20 sccm, Time: 6 min, RF power: 99, Ref: 0.3, DC: 230, Temperature: RT, Etching rate: 62 nm/min.
7	Purge N ₂	Pressure: 400 mTorr, Time: 5 min
8	Final pump	Pressure: 4 mTorr, Time: 5min, RT

Table S7 PECVD definition for Oxygen-plasma treatment

Step No.	Step description	Parameters
1	Pump down	Pressure: 5 mTorr, Time: 1 min, RT
2	High vac turbo pump	Pressure: 1.0×10^{-11} , Time: 3 min, RT
3	Gas stabilization I	180 mTorr, O ₂ : 50 sccm, Time: 30 s, Temperature: RT
4	Gas stabilization II	180 mTorr, O ₂ : 40 sccm, Time: 30 s, Temperature: RT
5	Gas stabilization III	180 mTorr, O ₂ : 30 sccm, Time: 30 s, Temperature: RT
6	Oxygen-plasma process	180 mTorr, O ₂ : 30 sccm, Time: 5 min, RF power: 60, Ref: 0.0, DC: 146 Temperature: RT,
7	Purge N ₂	Pressure: 400 mTorr, Time: 3 min
8	Final pump	Pressure: 3 mTorr, Time: 3min, RT

Table S8 E-beam deposition metal films (Ni, Ti) by Edwards Auto 306

Deposition Sequence	Layer 1	Layer 2
Materials	Ni	Ti
Base Pressure	4.6e-6	6e-7
Deposition Pressure	9.0e-6	1.1e-6
Beam Current (mA)	100/110	65
Voltage (kV)	4.73	4.73
X Sweep Freq.	15	15
Y Sweep Freq.	15	15
Dep. Rate (nm/sec.)	0.01	0.03
Density	8.91	4.5
Z-Value	26.7	14.1
Tooling Factor	0.55	0.55
Terminate (nm)	100	100

Table S9 E-beam deposition metal films (Ag, Pd) by Edwards Auto 306

Deposition Sequence	Layer 1	Layer 2
Materials	Ag	Pd
Base Pressure	8e-7	2.7e-6
Deposition Pressure	2e-6	4.8e-6
Beam Current (mA)	14	53
Voltage (kV)	5	5
X Sweep Freq.	15	15
Y Sweep Freq.	15	15
Dep. Rate (nm/sec.)	0.13	0.1
Density	10.5	12
Z-Value	16.7	29.7
Tooling Factor	0.48, 0.55	0.8
Terminate (nm)	100	100

Table S10 E-beam deposition metal films (Cr, Cu) by Edwards Auto 306

Deposition Sequence	Layer 1	Layer 2
Materials	Cr	Cu
Base Pressure	7e-7	1.5e-6
Deposition Pressure	2e-6	1.3e-6
Beam Current (mA)	43	47
Voltage (kV)	4.5	5
X Sweep Freq.	15	15
Y Sweep Freq.	15	15
Dep. Rate (nm/sec.)	0.1	0.2
Density	7.2	8.9
Z-Value	28.9	20.2
Tooling Factor	1	1
Terminate (nm)	100	100

Table S11 E-beam deposition metal films (Au, Ge) by Edwards Auto 306

Deposition Sequence	Layer 1	Layer 2
Materials	Au	Ge
Base Pressure	6e-6	2.0e-6
Deposition Pressure	4.6e-6	2.3e-6
Beam Current (mA)	62	30
Voltage (kV)	4.6	4.6
X Sweep Freq.	15	15
Y Sweep Freq.	15	15
Dep. Rate (nm/sec.)	0.1	0.1
Density	19.3	5.35
Z-Value	23.2	0.52
Tooling Factor	1	1
Terminate (nm)	100	100

Table S12 E-beam deposition metal films (ITO, MoO₃) by Edwards Auto 306

Deposition Sequence	Layer 1	Layer 2
Materials	ITO	MoO ₃
Base Pressure	1.8e-6	1.8e-6
Deposition Pressure	1.4e-6	3e-6
Beam Current (mA)	3-4	13-14
Voltage (kV)	4.6	4.5
X Sweep Freq.	15	15
Y Sweep Freq.	15	15
Dep. Rate (nm/sec.)	0-0.1	0.07
Density	4.7	7.1
Z-Value	20.1	20.1
Tooling Factor	1.0	1.0
Terminate (nm)	100	100

PlasmaTherm 790 Recipe Summary (for PECVE Chamber recipe)

No.	Process Description	Process ID	Conditions	Comments
1	Silicon dioxide deposition (FN: sio2dep)	SiO ₂	SiH ₄ =100 sccm; N ₂ O=30 sccm; N ₂ =600 sccm; Pressure=800 mTorr; RF power=60 W; Temperature:300°C	Deposition Rate=66 nm/min
2	Silicon Nitride deposition (FN: sindep)	SIN	SiH ₄ =100 sccm; NH ₃ =20 sccm; N ₂ =600 sccm; Pressure=800 mTorr; RF power=40 W; Temperature:300°C	Deposition Rate=31 nm/min
3	Low-temperature silicon dioxide deposition (FN: ltsio2dep)	LTSiO ₂	SiH ₄ =100 sccm; N ₂ O=30 sccm; N ₂ =600 sccm; Pressure=800 mTorr; RF power=60 W; Temperature:50°C	Deposition Rate=53nm/min
4	LT Silicon Nitride deposition (FN: ltsindep)	LTSIN	SiH ₄ =100 sccm; NH ₃ =20 sccm; N ₂ =600 sccm; Pressure=800 mTorr; RF power=40 W; Temperature:50°C	Deposition Rate=31 nm/min
5	Chamber Cleaning (FN: rclean)	RCLEAN	CF ₄ =40 sccm; O ₂ =30 sccm; Pressure=150 mTorr; RF power=150 W; Temperature:50°C	Default time: 30 min

PlasmaTherm 790 Recipe Summary (for RIE Chamber recipe)

No.	Process Description	Process ID	Conditions	Comments
1	Silicon dioxide etching (FN: sio2etch)	SiO ₂ etch	CF ₄ =50 sccm; O ₂ =20 sccm; Pressure=80 mTorr; RF power=100 W; Temperature: 25°C	Etching Rate=31 nm/min
2	Silicon Nitride etching (FN: sinetch)	SINEtch	CF ₄ =10 sccm; O ₂ =5 sccm; Pressure=30 mTorr; RF power=40 W; Temperature: 25°C	Etching Rate=33 nm/min
3	Chamber Cleaning (FN: rclean)	RCLEAN	CF ₄ =40 sccm; O ₂ =30 sccm; Pressure=150 mTorr; RF power=150 W; Temperature: 50°C	Default time: 30 min

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