NANOWIRE AND GRAPHENE-BASED VAPOR SENSORS FOR ELECTRONIC NOSE APPLICATIONS

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To My Parents
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ABSTRACT

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The development of a sophisticated electronic nose (E-nose) system would open vast markets spanning a wide variety of applications. Despite several decades of intensive research, the goal of creating such an E-nose system has yet to be achieved. The major difficulty is to create a sensor array with the extremely large chemical diversity and massive parallelism that is characteristic of mammalian olfactory systems. In this thesis, we have moved one step closer to this goal by synthesizing, characterizing and integrating heterogeneous nanowires on chip.

The work presented in this thesis is divided into three parts with the first part focused on single nanowire chemical gas sensors, the second part on heterogeneous nanowire integration and the third part on graphene vapor sensors.

In the first part of work, we synthesized single nanowire sensors of conducting polymers (PEDOT/PSS) and metal oxides (TiO₂) using electrochemical-templating method. The electronic and gas-sensing properties including thermal effects of these nanowires were also investigated. This part of work laid a solid foundation for the nanowire integration in the second part of work.
The second part started with analysis of the challenges to develop a sophisticated E-nose system. To address these challenges, we proposed and demonstrated a novel electrochemical approach by integrating silver, gold, tin and TiO₂ two- and multiple terminal nanowires on chip. This approach has a potential to realize such a sophisticated E-nose system.

The third part of work is to explore properties of graphene sensors. We found that the contamination layer left by conventional nanolithographic processing both degraded the electronic properties of the graphene and masked graphene's intrinsic sensor responses. The contamination layer chemically doped the graphene, enhanced carrier scattering, and acted as an absorbent layer that concentrated analyte molecules at the graphene surface, thereby enhancing the sensor response. We demonstrated a cleaning process that verifiably removed the contamination on the device structure and allowed the intrinsic chemical responses of graphene to be measured.
Contents

1 Overview ........................................................................................................................................... 1

2 Introduction ....................................................................................................................................... 4

  2.1 Conducting Polymers ...................................................................................................................... 4

    2.1.1 History of Conducting Polymers ............................................................................................... 4

    2.1.2 Conduction Mechanism ............................................................................................................ 5

    2.1.3 PEDOT/PSS ............................................................................................................................... 7

  2.2 Conduction and Sensing Mechanism of Metal Oxides ................................................................. 8

  2.3 Activation Energy and Band Gap ................................................................................................... 10

  2.4 Nanowire Synthesis Methods ....................................................................................................... 12

  2.5 Principle of Electrochemistry ....................................................................................................... 16

  Summary .............................................................................................................................................. 21

3 Conducting Polymer and Metal Oxide Nanowire Sensors .................................................................. 22

  3.1 Nanowire Synthesis by Electrochemical-Templating Method ....................................................... 23

    3.1.1 Synthesis of Conducting Polymer Nanowires ........................................................................... 24

    3.1.2 Synthesis of Metal Oxide Nanowires ....................................................................................... 27

    3.1.3 Synthesis of 3-D TiO2 Photonic Crystals and Sandwiched TiO2 particles .............................. 29

  3.2 Device Fabrication ....................................................................................................................... 30

    3.2.1 Dielectrophoretic Assembly .................................................................................................... 31
5.5 Intrinsic Response of Graphene Vapor Sensors .................................................. 85

Summary ......................................................................................................................... 92

6 Summary and Future Work .......................................................................................... 94

6.1 Summary ................................................................................................................. 94

6.2 Future Work ............................................................................................................ 96

Bibliography ................................................................................................................... 99
List of Figures

2-1 Band structure of doped conducting polymers ........................................ 6
2-2 Microstructures of conducting polymers ................................................ 6
2-3 Molecular structures of PEDOT and PSS ................................................ 7
2-4 Cross-sectional view of the schematic morphological model for PEDOT:PSS thin films ................................................................. 8
2-5 Band structure and microstructure of polycrystalline and single-crystalline nanowires ................................................................. 9
2-6 Activation energy of single crystal nanowires and polycrystalline nanowires.... 10
2-7 Absorption rate vs incident photon energy .............................................. 12
2-8 The furnace diagram of LVS nanowire synthesis method ......................... 13
2-9 A gold catalyst particle on the tip of a ZnO nanowire ............................. 14
2-10 Schematic of a 3-probe electrochemical system and its equivalent circuit .... 17
2-11 Configuration of the constant current mode ......................................... 18
2-12 Configuration of the constant voltage mode ......................................... 19
2-13 A typical cyclic voltammogram ........................................................... 21
3-1 Electrochemical Templating Method .................................................... 23
3-2 SEM image of a “striped” PEDOT/PSS nanowire and molecular structure of PEDOT/PSS ................................................................. 25
3-3 Synthesis of TiO₂ nanowire by electrochemical templating method .......... 26
3-4 SEM image and EDX spectrum of TiO$_2$ nanowires ........................................ 28

3-5 SEM images of 3-D TiO$_2$ photonic crystals and sandwiched TiO$_2$ nanoparticles ................................................................. 29

3-6 SEM image of a TiO$_2$ nanowire device .................................................. 30

3-7 Dielectrophoretic assembly process ...................................................... 33

3-8 Circuits for single nanowire assembly .................................................. 33

3-9 An array of assembly circuits on glass slide ......................................... 34

3-10 Assembly circuits based on the commercial .18\mu m Technology and SEM image of nanowires assembled in an array ......................................................... 36

3-11 IV curves of a single TiO$_2$ nanowires at different temperatures ............. 36

3-12 Activation energy of TiO$_2$ nanowires .............................................. 37

3-13 Current-voltage characteristic of a single polymer nanowire .................. 38

3-14 Resistance v.s. length/(cross-sectional area) l/A is plotted for 14 samples .... 40

3-15 Gas delivery system ........................................................................... 40

3-16 Response of a single TiO$_2$ nanowire to 20% O$_2$ .................................... 42

3-17 Nanowire sensor responses to methanol, ethanol and acetone .............. 44

3-18 Sensor response to ethanol vapor of various concentrations at elevated temperatures .................................................................................. 45

3-19 Interpretation of the physical implication of $\beta$ .................................... 46

3-20 Repeatability of nanowires .................................................................. 48

4-1 The olfaction of human noses and electronic noses .................................. 51
5-4 Steps of depositing graphene on silicon substrate ........................................... 76
5-5 Open an optical image in ELPHY Quantum .................................................. 78
5-6 Load an optical microscopic image into a pattern design file ......................... 79
5-7 An optical image loaded into a pattern design file as the background .............. 79
5-8 Virtual alignment markers are drawn on gold alignment markers ..................... 81
5-9 Current vs. Voltage of a graphene transistor .................................................. 82
5-10 Conductivity of Voltage of the same device ................................................. 84
5-11 The resistivity originated from long-range and short-range scatterings .......... 85
5-12 AFM image, schematic, thickness profile and gate effect of a graphene
    transistor ............................................................................................................. 86
5-13 Measured sensor response before and after the sample cleaning ...................... 89
Chapter 1
Overview

The development of a sophisticated electronic nose (E-nose) system would open vast markets spanning a wide variety of applications\textsuperscript{1,2}, such as clinical assaying, emission control, explosive detection, agricultural storage and shipping, and workplace hazard monitoring. Despite several decades of intensive research, the goal of creating such an E-nose system that can compete with a biological olfactory system has yet to be achieved. The major difficulty to reach this goal is the creation of a sensor array with the extremely large chemical diversity and massive parallelism that is characteristic of mammalian olfactory systems. For example, the human nose has more than 400 different types of sensing cells and each type is replicated over 100,000 times, for a total of around forty million cells overall.\textsuperscript{2} The traditional technologies face a huge obstacle to make such a sensor array in terms of the scale and chemical diversity.

To address this challenge, we first synthesize conducting polymer and metal oxide nanowire sensors using electrochemical-templating method. The electronic and gas-sensing properties of these sensors are also investigated in this part. We then propose and demonstrate a new approach that can integrate together all the aforementioned nanowire sensors using the same electrochemical synthesis method. This approach has a potential to create a sensor array with the extremely large chemical diversity and massive parallelism. Finally, we explore the electronic and gas-sensing properties of single-layer
Chapter 2 covers the background knowledge including the historic discovery and conduction mechanism of conducting polymers, the conduction and activation energy of metal oxides, the principle of electrochemistry, and an overview of nanowire synthesis.

In Chapter 3 we will synthesize two categories of nanowire sensors: conducting polymers and metal oxides. We then fabricate nanowire sensor devices by electron beam lithography (EBL) and dielectrophoretic assembly. The electronic and gas-sensing properties of these nanowires sensor will also be investigated.

In Chapter 4 we first analyze challenges for development of electronic nose systems and then review current technological progress that has a potential to address these challenges. As the most important part of this chapter, a novel on-chip electrochemical templating approach is proposed to provide a full solution for all these challenges. This chapter continues to demonstrate the idea by fabricating the on-chip nanochannel template and integrating Ag, Au, Sn and TiO₂ two terminal and multiterminal nanowires. At the end of this chapter, integration of CMOS circuits with heterogeneous nanowire arrays is designed and the microhotplate technology is proposed to solve the operation temperature incompatibility of CMOS circuits and nanowire sensors.

In Chapter 5 we explore the properties of graphene, a single layer of graphite which is a new hot material exfoliated from bulk graphite in 2004. This chapter will first briefly introduce the history and properties of graphene and then illustrate the mechanical exfoliation of graphene sheets. The fabrication of graphene devices using electron beam
lithography will be discussed in details, which is followed by extraction of charge carrier mobility in graphene from I-Vg curves. The electronic and gas-sensing properties will be presented in the end.
Chapter 2

Introduction

This chapter covers the background knowledge including the historic discovery and conduction mechanism of conducting polymers, the conduction and activation energy of metal oxides, the principle of electrochemistry, and an overview of nanowire synthesis.

2.1 Conducting polymers

2.1.1 History of Conducting Polymers

It is generally accepted that conducting polymers were discovered by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa in the early 1970s who were awarded Nobel Prize in the year 2000 for this discovery. Before this, most conducting polymers were widely known in their nonconductive forms. Though some conducting polymers were found to be conducting, this property did not attract much attention. For example, the first report of conducting polymers was as early as in 1862. This discovery was lost and picked up in 1910’s and 1960’s after further investigation. After the revolution of silicon technology starting in 1960’s, people acknowledged the importance of the conductivity of materials. Once the three scientists Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa found the incredible increase of ten million times the original conductivity after oxidation of polymer polyacetylene, people realized that conducting polymers as a new material, very different from inorganic semiconductors, might ignite a
new technology revolution. Since then conducting polymers have attracted intensive research interests, for example, within ten years from 1991 to 2000, 4888 papers published on conducting polymers involving 7959 authors, 76 countries, 458 journals and 1480 organizations. So, strictly speaking, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa “rediscovered” conducting polymers.

In the last three decades, electronic, chemical, mechanical and optical properties of conducting polymers have been thoroughly investigated. Due to the unique properties, conducting polymers have been widely used as static and anticorrosive coatings, chemical gas sensors, photo diodes, organic transistors, solar cells and artificial tissues. The most impressive application could be the flexible display commercialized in recent years.

2.1.2 Conduction Mechanism

The conduction mechanism of conducting polymers is still in dispute and only a rough picture is presented here. Refer to more papers for details.

The conductivity of bulk conducting polymers is originated from the transport of charge carriers both along and between polymer chains. Crystalline conducting polymers have spatially delocalized π and π* orbitals extended over the entire crystal, from which valence and conduction band are originated, respectively. Intrinsic conducting polymers have a wide bandgap and thus are highly resistive. “Doping” by reducing or oxidizing the polymers will introduce bipolaron bands which are located within the bandgap. These
bands of heavily doped conducting polymers will eventually overlap with the valence and conduction bands, which leads to metallic conductivity of the polymers.

\[ E_c \]

\[ E_v \]

Intrinsic \hspace{1cm} Less Doped \hspace{1cm} Highly Doped

Figure 2-1 Band structures of conducting polymers.

However, in reality, bulk conducting polymers are generally polycrystalline with crystalline islands connected to each other by randomly distributed polymer chains, as shown in Fig.2-2.

The randomly distributed polymer chains form an amorphous medium and act like a quantum dot between the crystalline islands. Within crystalline islands, the electron wave function extends over the entire island. In this case, the islands can be considered as metallic grains embedded in the amorphous poorly conducting matrix. Charge carriers transporting from one island to another through the random polymer chains follow
2.1.3 PEDOT/PSS

Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT) was discovered by scientists at Bayer AG research laboratories in Germany during the second half of the 1980s. PEDOT was initially found to be an insoluble polymer and therefore hard to process. However, it exhibited some very interesting properties such as highly conductive, almost transparent and stable in the oxidized state. In order to solve the solubility process, a water-soluble polyelectrolyte poly(styrenesulfonic acid) (PSS) was added as a charge-balancing dopant during polymerization. The resulted PEDOT/PSS combined the properties of PEDOT and PSS, obtaining good film-forming properties, high conductivity, high visible light transmissivity, and excellent stability.

Like other typical conducting polymers, PEDOT/PSS can be synthesized by chemical polymerization or electro-polymerization. Chemically polymerized PEDOT/PSS has a low conductivity ($10^{-4}-1$ S/cm). In microscale, PEDOT and PSS are more like two phases mixing together (Fig.2-4), leading to an unstable composition.
upon the process environment. For example, a mild water washing can bring away a large amount of PSS. In contrast, electro-polymerized PEDOT/PSS has a stable chemical composition since the PEDOT and PSS polymer chains are chemically bonded together\textsuperscript{35}, which is similar to other typical doped conducting polymers.

![Cross-sectional view of the schematic morphological model for PEDOT:PSS thin films.](image)

Figure 2-4 Cross-sectional view of the schematic morphological model for PEDOT:PSS thin films. PEDOT-rich clusters (dark) are separated by lamellas of PSS (light). The PEDOT-rich lamella is composed of several pancake-like particles as pictured by the dotted lines. The typical diameter $d$ of the particles is about 20-25 nm and the height $h$ is about 5-6 nm. The figure is from ref. \textsuperscript{34}

2.2 Conduction and Sensing Mechanism of Metal Oxide Sensors

Metal oxide sensors are usually large bandgap semiconductors and they are typically n-type due to their intrinsic defects.\textsuperscript{36} For example, in many cases titanium oxide is an n-type semiconductor due to its excess oxygen vacancies.\textsuperscript{36} These n-type metal oxides can be tuned to be intrinsic if properly doped with p-type dopants.\textsuperscript{37} Metal oxides in a form of thin films cannot form single crystals due to crystal mismatch from the substrate and therefore they are polycrystalline with many crystalline grains in most cases. In the past decade, it has been found that metal oxides synthesized in a shape of nanowires can
be a single crystal or polycrystalline depending on synthesis methods. Metal oxide nanowires synthesized by liquid-vapor-solid method (LVS)\textsuperscript{38} at a high temperature are single crystalline while those made by electrochemical templating method are polycrystalline in most cases.\textsuperscript{39}

![Figure 2-5 Microstructure of (a) polycrystalline and (b) single-crystalline nanowires](image)

Single-crystal metal oxides share the same conduction mechanism with a typical silicon semiconductor, shown in Fig.2-5b. The potential barrier induced the grain boundary exists only on the edge of the single crystal but not in the transport path of charge carriers. However, metal oxides are polycrystalline in many cases. Their conduction mechanism is complicated due to grain boundaries existing in the transport route of charge carriers (Fig.2-15a). The tangling bonds near the grain boundaries are potential barriers that charge carriers have to overcome by tunneling or thermal excitation.
When exposed to analytes, charge transfer will occur between the analyte molecules and the grain surfaces (Fig.2-5a). This charge transfer will increase or decrease the potential barrier (also the depletion region extended into bulk) of the grain boundaries. As for single crystals, it is the depletion region extended into crystalline bulk that is changed. In another word, the charge transfer alters the effective cross-area of the channel that charge carriers transport through. In this case, analyte molecules act like a gate that can tune the size of the transport channel. This is so-called “chemical gating effect”\textsuperscript{40, 41} (Fig.2-5b). As for poly-crystals (Fig.2-5a), the potential barriers exist in the transport path of charge carriers. Charges transferred from or to analyte molecules will alter the heights of potential barriers that charge carriers (electrons and holes) have to overcome. The overall resistance of the poly-crystal is therefore altered. Chemical gas sensors that operate by detecting the resistance change induced by analyte molecules in this way are called “chemiresistors”.

Figure 2-6 Band structures of single crystal nanowires and polycrystalline nanowires.
2.3 Activation Energy and Bandgap

Activation energy for solid-state devices often refers to thermal activation energy $E_a$ which is the energy required to thermally activate electrons (holes) from Fermi energy to conduction (valence) band for n-type (p-type) semiconductors. When Fermi energy is located in the center of bandgap, $E_a$ is a half of the bandgap. Otherwise, $E_a$ is smaller than half of the bandgap. For single crystal semiconductors, $E_a$ is the smallest distance that Fermi energy is located from bandgap edges (Fig. 2-6). For this reason, we have the conductivity of the device \[ \sigma = \sigma_0 \exp \left( -\frac{E_a}{kT/q} \right) \] from which the activation energy can be extracted\(^2\). However, for polycrystalline semiconductors especially when the grain size is in a nanometer scale and surface states are not negligible compared to bulk carrier states, a fair amount of charge carriers can be activated through surface states and the activation energy will become smaller due to the surface states.

By measuring the activation energy, we have no clue about the semiconductor bandgap which however can be extracted from the optical absorption spectra. For semiconductors that have a band gap of $E_g$, the absorption coefficient $\alpha$ follows the equation \[ \alpha h\nu_{in} \sim (h\nu_{in} - E_g)^\gamma \] where $\gamma = 1/2$ for direct bandgap semiconductors or $\gamma = 3/2$ for indirect bandgap semiconductors.\(^4\) The incident light will not be absorbed in theory when the energy of incident light is less than the bandgap. Only when the energy of the incident light is greater than the bandgap will the light be absorbed at a rate $\alpha$ that follows \[ (\alpha h\nu)^2 \sim h\nu_{in} - E_g \] (red line in Fig. 2-7) in the case of direct bandgap
semiconductors. Extending the straight line to zero absorption will intercept x coordinate at a specific energy which is the bandgap of the material. When the incident light has a lower energy than the bandgap, the absorption is not zero (Fig.2-7) due to absorption from impurity states, defect states and surface states located inside the bandgap.

![Figure 2-7 Absorption rate vs incident photon energy](image)

2.4 Nanowire Synthesis Methods

More than ten distinct methods of nanowires synthesis have been demonstrated to date. Two common and versatile methods are widely used to synthesize nanowires for sensing applications: the vapor-liquid-solid method (VLS) and the templating method. The VLS method is typically accomplished in a low pressure, high temperature furnace. It has been employed to synthesize metal oxide and semiconducting nanowires. The templating method is based on electrochemically depositing materials into a template.
structure consisting of aligned parallel nanopores. We are going to use conducting polymer PEDOT/PSS nanowire and metal oxide TiO$_2$ nanowires as examples to demonstrate this method in Chapter 2. In this section, only VLS will be discussed.

![Diagram of VLS nanowire synthesis method](image)

Figure 2-8 The furnace diagram of LVS nanowire synthesis method.

Vapor-liquid-solid (VLS) method is a commonly used procedure to synthesize nanowires. Nanowires consisting of In$_2$O$_3$\textsuperscript{44}, Ga$_2$O$_3$\textsuperscript{58}, SnO$_2$\textsuperscript{46}, ZnO\textsuperscript{47}, WO$_3$\textsuperscript{59}, TeO$_2$\textsuperscript{60}, V$_2$O$_5$\textsuperscript{48}, ZnSnO$_3$\textsuperscript{61}, Ge\textsuperscript{62} and Si\textsuperscript{49} have been grown using this method, among the other materials. The growth process is typically accomplished in a low pressure, high temperature furnace (Fig.2-8). The temperature near the source is elevated sufficiently to melt the source material so they may evaporate. A carrier gas flow brings the vapor to the substrate where nanowires grow with the assistance of catalysts. The catalyst material may be pre-deposited on the growth substrate, or it may form spontaneously during the VLS growth process, as described below.

VLS growth methods can be categorized according to the dominant physical-chemical growth process and the growth system. In terms of process, it can be classified as metal catalyst or non-metal catalyst (e.g., oxide or sulfide) VLS. The growth
system used is typically either thermal evaporation, laser ablation or inductive heating assisted synthesis.

![Image of a gold catalyst particle on the tip of a ZnO nanowire](image)

Figure 2-9. A gold catalyst particle on the tip of a ZnO nanowire (The figure from Ref. 63).

The metal catalyst VLS method uses metals such as Au, Fe, Co and Ni as catalysts. The metal catalysts can be mixed with the source material or spread on the substrate where the nanowires grow. In either case, the metal catalyst is either patterned or self-organized into nanoparticles (NPs). These NPs react with the source vapor forming solution droplets on the substrate serving as a preferential site for absorption of reactant, since there is a much higher sticking probability on liquid vs solid surfaces. When the droplets become supersaturated, they are the nucleation sites for crystallization. Preferential 1D growth occurs in the presence of reactant as long as the catalyst remains liquid. During this process, the catalyst particle tends to remain at the tip of the growing nanowire (Fig. 2-9). See Ref. 63 for details.

The size of the catalyst particles that are used to generate the nanowires depends on the preparation process. Typical methods include thin film deposition of the metal
catalyst on the substrate by thermal evaporation or sputtering. The metal thin film will cluster into small particles when heated up to the growth temperature. This typically leads to a wide distribution in NP diameter that is reflected in the diameter distribution of the resultant nanowires. The second approach is to deposit prefabricated monodisperse catalyst nano-particles on the substrate. Since the prefabricated nano-particles are uniform in size, nanowires can grow more uniformly in diameter.

Commonly used carrier gases include argon and nitrogen. Oxidizing gases may be mixed in the carrier gas, depending on the source material and the desired composition of the nanowires. For example, when growing metal oxide nanowires with the metal powder source, O₂ is often mixed in the carrier gas.

Oxide-assisted and sulfide-assisted growth are non-metal catalyst VLS which have been reported to prepare Si, GaAs, MgO nanowires. The oxide (or sulfide) played a critical role through the nanowire growing process. For example, it was observed that source material consisting of silicon blended with silicon oxide led to the growth of high-quality silicon nanowires, but growth of the resulting nanowires could not be continued using a pure silicon source. Although the exact mechanism of this synthesis remains unknown, the following explanation is believed to be plausible. The sub-oxide SiOₓ (x<2) vapor from the silicon source blended with SiO₂ is liquefied and eventually becomes supersaturated at the cooler substrate. Oxygen atoms are expelled from the supersaturated liquid and form a silicon dioxide shell layer surrounding a pure silicon crystal. However, the tip of the nanowire, somehow, remains silicon sub-oxide SiOₓ.
(x<2), which leads to the continuing (directional) growth of nanowires, while SiO$_2$ on the shell stops the nanowire from growing laterally. A pure silicon source without the SiO$_2$ catalyst cannot continue this process.

If we categorize the LVS method in terms of the preparation system, it can be classified as thermal evaporation\textsuperscript{45}, laser ablation\textsuperscript{43} and inductive heating assisted synthesis\textsuperscript{70}, which differ only in the heating source. Some of the heating sources have advantages over the others. For example, laser ablation may enhance the uniformity of the nanowire diameter\textsuperscript{43}. The inductive heating assisted synthesis can be more effectively heating up samples than the conventional thermal evaporation, which leads to a much shorter synthesis time\textsuperscript{70}.

2.5 Principle of Electrochemistry

In Chapter 3, we will discuss in details how to synthesize conducting polymer and metal oxide nanowires using electrochemical-templating method. Here a general introduction to electrochemistry will be presented.

The occurrence of chemical reactions needs to overcome the potential barrier between two chemical molecules. When the potential barrier is zero or negative, a chemical reaction will happen without any assistance and release energy after the reaction. If potential barrier is positive, external energy is required to initiate the reaction. The reaction eventually may release or absorb energy. Electrochemical reaction is the one in aqueous state that is assisted by electrical energy. The potential barrier for different
chemical reactions will be different. By carefully controlling the voltage assisting chemical reactions, one can favorably choose one reaction while suppressing others.

However, using a simple two-terminal circuit is difficult to precisely control the voltage due to parasitic contact resistance (between counter electrode and electrolyte) and the resistance of the electrolyte that are changing over time during the electrochemical process.

![Diagram of a 3-probe electrochemical system](image)

Figure 2-10 (a) Schematic of a 3-probe electrochemical system. The counter electrode (usually Pt) is anode and the working electrode is cathode. The current flows from counter to working electrode. Reference electrode reads out voltage and negligible current flows through it. (b) equivalent circuit of (a)

In order to control the voltage over the interface between electrolyte and working electrode where chemical reactions are happening, a reference electrode is added into the two-terminal circuits (Fig. 2-10a) whose equivalent circuit is shown in Fig.2-10b. Rc1 represents for the contact resistance between the counter electrode and electrolyte, r1, r2 and r3 stand for the resistances of electrolyte. Rc2 is the resistance of chemical reactions,
Rc3 is the contact resistance between reference electrode and electrolyte.

An electrical circuit is designed to guarantee a negligible amount of current flowing through the reference electrode. Therefore the reference electrode senses a voltage \( V = I \times r_2 + I \times Rc_2 \approx I \times Rc_2 \) because most electrolytes have a high concentration of ions and hence very conductive which leads to \( I \times r_2 \approx 0 \). A CMOS operational amplifier connected in a unity gain mode can read out the voltage on the reference electrode with zero current flow, shown in Fig. 2-11.

![Figure 2-11 Configuration of the constant current mode](image)

The electrochemical system can work in two modes: constant current (galvanostat) mode and constant voltage (potentiostat) mode. Figure 2-11 shows a constant current mode in which a constant current is flowing from the counter electrode and the voltage on the chemical reaction is read out. In a constant voltage mode, we can set the voltage that induces chemical reactions and therefore we can manipulate chemical reactions. The
control circuit for constant voltage mode employing a negative feedback circuit is more complicated, shown in Fig.2-12. Suppose current and voltage in Fig.2-12 are all zero. Let's suddenly set $V=1\text{V}$. The positive differential input on the op amp will ramp up its voltage and current output. The increasing current $I$ will elevate the voltage on $R_{c2}$ till the reference electrode has sensed a voltage equal to $1\text{V}$ (equal to the set $V$). In this way, we impose our set voltage on the chemical reaction.

![Figure 2-12 Configuration of the constant voltage mode](image)

What needs to explain more is that the resistors $R_{c1}$, $R_{c2}$ and $R_{c3}$ in Fig.2-10, 11 and 12 actually represent potential barriers. When current flows, these barriers can be modeled as nonlinear resistors. For different electrolytes, these potential barriers are different. Since $R_{c2}$ represents the chemical reaction, this makes the very sense because chemical reactions will be different for different electrolytes. $R_{c1}$ represents the potential
barrier between the counter electrode (usually Pt) and the electrolyte. Rc1 will also be different for different electrolytes. But it does not play a role in reading or setting either voltage or current. The potential barrier that Rc3 represents will offset the voltage input of the CMOS op amp. This potential barrier also different for different electrolytes will introduce some uncertainties in reading or setting voltage on chemical reactions. This undesirable effect can be avoided by using a specially designed reference electrode that has a metal wire in a salt solution (Ag/AgCl, for example). A salt bridge formed between the salt solution and the electrolyte brings in a zero offset. The metal wire in the salt solution introduces a constant voltage offset \( V_{\text{ref}} \) that is independent of the electrolyte. Therefore, we may not know the exact voltage on the chemical reaction but we definitely know it is a value minus a constant offset for any electrolyte.

As stated previously, constant voltage mode can pick up a specific chemical reaction by controlling the voltage over the chemical reaction that is happening on the working electrode. For a new chemical reaction, sweeping the voltage (reference voltage) over the chemical reaction can help us find the right voltage value for this reaction. The current is changing in real time when sweeping reference voltage. A plot of the current vs. reference voltage is called voltammogram. The current will reach its maximum at a voltage that assists the right chemical reaction by oxidizing or reducing. The reaction is usually reversible if sweeping back the voltage. For completeness, cyclic voltammograms are performed in most cases. A typical cyclic voltammogram is shown in Fig.2-13. The current peaks indicate the redox reactions. The heights of these peaks are dependent on
the sweeping rate of reference voltage due to ion diffusion in the electrolyte. Higher sweeping rates lead to higher current peaks.

Figure 2-13 A typical cyclic voltammogram

Summary

In this chapter, the conducting mechanisms of conducting polymers and metal oxides were illustrated, which were followed by the concept of activation energy. Vapor-Liquid-Solid, the most commonly used method for nanowire synthesis was then reviewed in detailed. The principle of electrochemistry was introduced in the end, which laid a foundation for the coverage of electrochemical-templating method which will be used to synthesize PEDOT/PSS and TiO₂ nanowires in this thesis.
Chapter 3
Conducting Polymer and Metal Oxide Nanowire Sensors

The development of a sophisticated electronic nose (E-nose) system would open vast markets spanning a wide variety of applications such as clinical assaying, emission control, explosive detection, agricultural storage and shipping, and workplace hazard monitoring. Clinical diagnostic applications alone represent a significant market that is driving a number of large research efforts in this area. For example, the acetone concentration in the breath of a healthy person is around 5 ppm, but increases to as high as 300 ppm for patients with diabetes mellitus. Mercaptans and aliphatic acids were found in the breath of patients with liver cirrhosis while dimethyl- and trimethylamine were found in that of uremic patients. The major challenge for development of such an electronic nose system is the construction of the “front end” of such a system: a sensor array with extremely large chemical diversity and massive parallelism.

Before constructing such a sensor array, we need to know the method for synthesizing the sensors and the properties of each sensor. Nanowire-based sensors are thought to present significant advantages over macroscopic bulk and thin-film analogues, such as significantly increased sensitivity and extremely high integration density. Therefore, in this chapter, we focus on this part by (i) synthesizing two categories of nanowire sensors: conducting polymers and metal oxides, (ii) fabricating nanowire sensor devices by electron beam lithography (EBL) and dielectrophoretic assembly, and (iii)
investigating their electronic and gas-sensing properties.

Figure 3-1 Electrochemical Templating Method. (a) Optical image of the setup; (b) Schematic of (a); (c) Diagram of Anodic Aluminum Oxide (AAO) template (d) SEM of the AAO template surface.

3.1 Nanowire synthesis by electrochemical-templating method

The electrochemical-templating method is a quite powerful approach to synthesize nanowires for use in electronic devices. It has been employed to synthesize nanowires consisting of metals,\textsuperscript{74} conducting polymers,\textsuperscript{18, 75} semiconductors\textsuperscript{57} and nonconductive metal oxides\textsuperscript{39}. In this thesis, we use this approach to synthesize and integrate nanowire sensors for E-nose applications that we are going to demonstrate. The idea of this method is to deposit materials into a nanoporous template by electrochemistry to form nanostructures (Fig.3-1). Nanoporous anodic aluminum oxide (AAO) membranes are the most extensively used templates for nanowire synthesis.\textsuperscript{39} The pores inside the membrane
are perpendicular to the surface and positioned in the form of a hexagonal lattice (See Fig.3-1d). The pore size is controlled by anodizing conditions such as anodizing voltage and concentration of acid. Currently AAO membranes with a pore size from 20nm to 200nm are commercially available from Whatman, Inc.

When synthesizing nanowires, the AAO membrane is first placed on a conducting electrode (it’s grounded as working electrode). In order to avoid nanowires connecting to each other through the gap between the membrane and the electrode, the membrane is always coated with a layer of evaporated silver (150nm thick) on the side contacting the electrode. A container filled with electrolytes is placed against the membrane and sealed by an o-ring (Fig.3-1a and b). Current is sourced through the counter electrode and electrochemical reactions occur at the interface between electrolyte and the working electrode. The reference electrode is placed inside the electrolyte to sense potential and no current flows through it. This system can work in Constant Current (CI) or Constant Voltage (CV) Mode. The circuit design for these two modes is shown in Section 2.5 and on the webpage: http://www.seas.upenn.edu/~yapingd/MyTech.htm.

Various types of nanowires used as chemical gas sensors have been synthesized with this method. Here, we focus our attention on conducting polymer and metal oxide nanowires.

3.1.1 Synthesis of conducting polymer nanowires
Conducting polymers are intriguing candidates for E-nose applications as they selectively respond to organic chemicals with high sensitivity under ambient conditions. Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) (Fig. 3-2b) received sustained interest in recent years as one of the most stable conducting polymers. It was used as the conductive component in a matrix of chemically different insulating polymers to form an array of vapor detectors. Inkjet-printed PEDOT/PSS films were also reported to be sensitive to methanol vapor. In this chapter, we first synthesize PEDOT/PSS nanowires and then assemble single nanowires dielectrophoretically. Electronic and gas-sensing properties will be investigated in the end.

To avoid the damage to PEDOT/PSS originated from photolithography or electron beam lithography (will be discussed in next chapter), we choose dielectrophoretic assembly instead of lithography to position these nanowires onto specific electrodes. In order to establish excellent contact with gold electrodes after dielectrophoretic assembly, the nanowires need to have a "striped" structure gold-polymer-gold, shown in Fig. 3-2a.
To synthesize these "striped" nanowires, the first Au segment of the nanowires was deposited galvanostatically using a commercial Au plating solution (Orotemp 24 from Technic Inc), followed by the growth of the polymer segment. The second Au segment was grown using electroless deposition and then elongated by electrodeposition galvanostatically. (Refer to ref 18 for details.)

After synthesis, the nanowires were released by dissolving the membrane in 500mM NaOH for ~1 h, and the solution was then purified by repeating the following steps 5 times: centrifuge (using Marathon 16000R) at 1000RCF (=1000×g) for 5 min, keep the bottom part of the solution and dilute it with deionized water. The nanowires were assembled from the solution onto specific locations using a home-built dielectrophoretic assembly apparatus that we will discuss in Section 3.2. SEM images of samples after assembly clearly show that nanowires with the desired "striped" geometry have been formed through the synthetic process (Fig.3-2a).

![Synthesis of TiO₂ nanowire by electrochemical templating method](image)

Figure 3-3 Synthesis of TiO₂ nanowire by electrochemical templating method

3.1.2 Synthesis of metal oxide nanowires
Metal oxide sensors are highly sensitive and have been commercialized for decades. To increase the diversity of sensor arrays, metal oxide sensors in addition to conducting polymers are also good candidates for E-nose application. However, it is not intuitive to synthesize metal oxide nanowires by electrochemistry since they are highly nonconductive at room temperature. Luckily chemists found some ways to circumvent this difficulty. One way is the so-called “sol-gel” technique. Here we use TiO$_2$ nanowires as an example to demonstrate how to synthesize metal oxide nanowires by electrochemistry.

We first dissolved high purity titanium (99.999%) in H$_2$O$_2$ and 30% NH$_4$OH with a volume ratio of 1:1. After approximately one week, the yellow so-gel TiO(OH)$_2$·xH$_2$O formed (left bottle in Fig.3-3). By adding H$_2$SO$_4$ acid into the bottle, the sol-gel was turned into a red solution (right bottle). These two solutions could be turned into each other back and forth by increasing pH (adding NH$_4$OH) or decreasing pH (adding H$_2$SO$_4$) across over 3. Before electrochemical synthesis, the solution was prepared with a pH value right below 3 (0.145M KNO$_3$ was also added to assist chemical reaction, refer to ref for more information). Inside one nanopores during the electrochemical synthesis, OH$^-$ ions induced by voltage showed up near the cathode, which locally increased the pH above 3 and turned the red solution into yellow sol-gel (left inset in Fig.3-3). This process continued and eventually the nanopores were filled up with the yellow TiO(OH)$_2$·xH$_2$O sol-gel.
Figure 3-4 The TiO$_2$ was crystallized after annealing at 400$^\circ$C in air (the up right inset). EDX spectrum indicates titanium exists in the nanowire. Silicon and part of oxygen signals from the substrate.

The whole template sample was then annealed at 450$^\circ$C for 24h in air, which turned the sol-gel into polycrystalline TiO$_2$. The TiO$_2$ nanowires were released by dissolving the membrane in 500mM NaOH for ~1 h and the solution was then purified in the same way as we purified conducting polymers.

An SEM image of a single TiO$_2$ nanowire is shown in the right inset of Fig.3-4. The wire is approximately several micrometers long and 150nm in diameter. The white end is gold which we incorporated for two purposes. First, it served as a buffer when we dissolved the silver thin film evaporated on the AAO template surface. As we discussed at the beginning of Section 3.1, this evaporated silver thin film served as the working electrode and it helped nanowires in different pores to be isolated from each other. Secondly, this gold end was much more visible than the nanowire itself when we did electron beam writing. It helped to identify the nanowire. EDX spectrum in Fig.3-4 has proven the nanowire is titanium oxide by showing titanium signals originated from the nanowire. Silicon and part of oxygen signals are from the SiO$_2$/Si substrate.
3.1.3 Synthesis of 3-D TiO₂ photonic crystals and sandwiched TiO₂ nanoparticles

In addition to the wire-shaped nanostructures, we also synthesized some more complicated structures of TiO₂ for other applications, for example, 3-D TiO₂ photonic crystals\textsuperscript{86} (Fig. 3-5b) that can be synthesized using the photoresist SU-8 template (Fig. 3-5a). This artificial crystal showed extraordinary photonic properties as we demonstrated in our papers.\textsuperscript{86}

Contacting a nanoparticle is always a big challenge. The electrochemical-templating method is an intriguing approach to address this issue. A TiO₂ nanoparticle sandwiched in a gold nanowire (Fig. 3-5c) can be synthesized in this way by growing Au-TiO(OH)₂-Au in sequence. The TiO(OH)₂ sol-gel can be crystallized after annealing at 450°C for 24 hours. Semiconducting nanoparticles in a similar structure have extraordinary properties
as transistors. Similar nanoparticles used as sensors may also be very intriguing.

3.2 Device Fabrication

We have successfully synthesized conducting polymer and metal oxide nanowires in Section 3.1. To characterize their electronic and gas-sensing properties, these nanowires need to be contacted with microelectrodes. Photolithography or electron beam lithography (EBL) can be used to fabricate the electrodes. In Figure 3-6, we employed EBL to make four microelectrodes (Pt/Cr) contacting a single TiO$_2$ nanowire.

![Figure 3-6 SEM image of a single TiO$_2$ nanowire contacted by four Pt/Cr electrodes fabricated by standard electron beam lithography](image)

However, we cannot make contact to conducting polymers this way because developers that attack polymers are involved in either photolithography or e-beam lithography. These lithography technologies also employ high-energy beam (UV or electron beam) to break the polymer chains (for positive resist) into fragments that can be
then dissolved by developers. Our PEDOT/PSS nanowires have polymer chains including conjugate ones that are also exposed to the damage from developers and/or high-energy beams. In experiments, we observed polymer nanowires made contact using these lithography technologies had a resistance ten times higher than their intrinsic resistance. One possible way to avoid the chemical or radiation damage to the polymer nanowire is to use patterned shadow masks and thermal evaporation so that lithography is avoided entirely. Critical dimensions well below 1 μm are achievable. Care is needed to ensure that heat generated from evaporating does not lead to degraded sensing performance of the polymer nanodevices. More importantly, fabrication of large arrays of nanowires can be problematic using shadow masks because it is not trivial to ensure proper alignment of the contacts and the nanowires.

In order to solve these problems, nanowires with a "striped" structure (Au-polymer-Au) were grown using a nanoporous template and multiple electrodeposition steps (see Section 3.1). The striped nanowires were then dielectrophoretically assembled onto prefabricated gold electrodes (see Section 3.2.1). The contact resistance between gold and polymer was intrinsic and relatively small since they were electrochemically synthesized. The two gold ends of the nanowire resulted in excellent, reproducible contact with prefabricated gold electrodes. This method guaranteed a minimum contact resistance and was successfully used to make an array of devices consisting of single nanowires.\(^8\)
3.2.1 Dielectrophoretic assembly

Before assembling nanowires, we first discuss how dielectrophoretic assembly works. Suppose a DC electric voltage is applied onto a pair of electrodes. Nanowires in this electric field (E-field) will be polarized (Fig.3-7a). The polarized nanowires have an electric force pulling them towards the gap between the electrodes where the highest E-field intensity is. However, in experiments, nanowires usually suspend in a medium such as DI water or Isopropanol (IPA) that will also be polarized in electric fields. The polarized medium forms a dipole opposite to the nanowire dipole (Fig.3-7b). There are three cases in such a scenario: (i) If the medium’s permittivity $\varepsilon$ is less than the nanowire’s, i.e. $\varepsilon_m < \varepsilon_n$, the force on the nanowire will be reduced; (ii) If $\varepsilon_m = \varepsilon_n$, the force on the nanowire will be reduced to zero; (iii) If $\varepsilon_m > \varepsilon_n$, the force on the nanowire will be reversed, which means the nanowire will be pushed away from the gap. Any of these three cases will be unfavorable to the nanowire assembly.

In order to avoid such a scenario, we apply an AC instead of DC voltage onto the gap. The permittivity of the DI water or organic medium decreases rapidly at high frequencies while that of the metallic conducting polymers does not. In an appropriate range of frequency, the polarization of the medium is reduced to a negligible amount (Fig.3-7c) and the force on the nanowire thus resumes. In experiments, we find nanowires can be readily assembled with an amplitude 20V peak-to-peak (Vpp) in a range from 100kHz to 1MHz. The AC voltage is usually sourced from a function generator. The electric field sustains even after the nanowire is assembled onto the gap (Fig.3-7d), which will results
in two unfavorable effects: (i) the assembled nanowire will be damaged by the 20Vpp voltage; and (ii) more nanowires will be assembled onto the same gap since the electric field sustains.

Figure 3-7 Dielectrophoretic assembly process. (a) A nanowire polarized in a DC electric field and the induced electrical static force will pull the wire to the gap; (b) In experiments, the nanowire usually suspends in a medium that will be polarized too. The electric force on the wire will be reduced, disappear, or even reversed if the permittivity of media is greater than that of the wire; (c) The permittivity of the medium decreases rapidly in a high frequency (100KHz-1MHz) AC electric field while that of the conducting wire will not. The electric force on the wire will resume in this case; (d) When one wire is assembled on the electrode gap, the electric field still sustains.

Figure 3-8 Circuits for single nanowire assembly. (a) schematic of two capacitors in series; (b) Electrical field distribution before and after assembly.
To avoid these unfavorable effects, we designed a circuitry shown in Fig. 3-8a. The device assembly site consisted of a pair of electrodes separated by approximately 5\(\mu\)m (the assembly capacitor). One of the two electrodes was capacitively coupled by an 8\(\mu\)m gap (the coupling capacitor) to a feed-in lead, and the second electrode was grounded. The coupling capacitor and assembly capacitor were designed to be approximately 200 fF and 10 fF, respectively.

![Diagram of circuitry](image)

Figure 3-9 (a) An array of assembly circuits (shown in b) fabricated on a glass slide using photolithography; (c) A close look of the assembly capacitors and coupling capacitors; (d) The array of the assembly circuits can be connected to a source meter through a commercial 8mm very high density connector (VHDC).

A voltage of 20 Vpp at a frequency of 100 kHz was applied across these two capacitors whose impedances at this frequency (8 M\(\Omega\) and 150 M\(\Omega\), respectively) are \(\approx\)100-1000 times greater than the polymer nanowires (~100 k\(\Omega\)). These impedance values imply that before assembly about 19 V drops across the assembly capacitor, leading to a
high electric field in this gap that draws nanowires into the desired location. After the first nanowire is brought into contact with both electrodes, the voltage drop across the assembly capacitor decreases to ~200 mV (Fig.3-8b), so the assembly process is self-terminating.

We fabricated an array of such circuits on a glass slide (Fig.3-9a and b). All the circuits shared one ground and assembly sites were close to the shared ground electrodes. The coupling capacitors were approximately 0.5cm away from the assembly sites. During assembly, an o-ring was placed between them to isolate nanowire suspensions from the coupling capacitors. Nanowires were assembled onto only the assembly sites. With samples consisting of an array of 30 such electrode pairs, we were able to assemble single-nanowire circuitry with a yield of 35 – 50%. After assembly, a small drop of silver paste was applied to short the coupling capacitor and enable dc electrical measurements. The long electrodes running to the edge were designed to 0.8mm apart. This design is compatible to the commercial .8mm Very High Density Connector (VHDC). Sliding the glass slide into the connector connected all the nanowires to source-meters through a multiplexer (Fig.3-9d).

We designed a similar circuits (Fig.3-10a, the coupling capacitors were buried underneath and refer to our paper for more information89) based on the .18μm technology and assembled gold nanowires on this real chip fabricated by a foundry.89 An SEM image of such an array of gold nanowires is shown in Fig.3-10b. The part of work has demonstrated that this dielectrophoretic assembly technique can be used to integrate a
large array of nanowire-based sensors onto a fully processed silicon CMOS chips. And data processing of the array output can also be accomplished in a compact, inexpensive package.

Figure 3-10 (a) Layout of the assembly circuits based on the commercial .18μm Technology; (b) An SEM image of nanowires assembled in an array.

![figure](image)

Figure 3-11 Two-probe measurement of a single TiO$_2$ nanowire (shown in the inset) at different temperatures.

3.3 Electronic properties of single nanowires
A single TiO$_2$ nanowire has been made contacted with using EBL and thermal evaporation and a single PEDOT/PSS nanowire has been electrically connected after assembly. We are ready to characterize their electronic properties.

3.3.1 TiO$_2$ nanowires

Titanium oxide has a wide bandgap (~3eV) and is highly resistive at room temperature without being heavily doped. At elevated temperatures, more charge carriers are readily activated to conductance or valence band and the nanowire thus becomes more conducting. For example, such a nanowire as shown in the inset of Fig.3-11 has a resistance over 10GΩ at room temperature and this value decreases to ~200MΩ after the temperature is elevated to 200°C.

![Graph](image)

Figure 3-12 The resistivity of the TiO$_2$ nanowire is correlated with the temperature, from which the thermal activation energy is extracted to be 0.5eV. The activation energy of a thin film can be extracted to be 0.6eV from the dashed line (from Ref. 37).
When we sweep the voltage on the nanowire from -5V to +5V, the current (Fig.3-11) shows a nonlinear behavior due to the nonlinear Schottky barrier between TiO$_2$ and Pt/Cr electrodes. We extract the conductivity $\sigma$ of the titanium oxide nanowire from the linear part of I-V curves and plot $\sigma$ vs 1000/T in Fig.3-12, where T is the absolute temperature. As we expected, $\sigma$ follows the equation

$$\sigma \sim \exp\left(\frac{qE_a}{kT}\right) \Rightarrow \ln(\sigma) \sim \frac{qE_a}{kT} \quad \text{Eq.(1)}$$

Thermal activation energy $E_a$ is extracted to be $\sim 0.5\text{eV}$ by fitting the data in Fig.3-12 into Eq.(1). This value is comparable to that of titanium oxide thin films ($0.6\text{eV}$ extracted from the blue line$^{90}$) that were prepared in a similar way as our TiO$_2$ nanowires were. Both of these values are much smaller than the thermal activation energy of single-crystal intrinsic titanium oxide which is supposed to be 1.5eV, a half of the bandgap. The impurities introduced in the synthesis process and surface states of the nano crystalline grains play a critical role in this small activation energy.

3.3.2 Conducting polymer nanowires

The inset of Fig. 3-13 shows a single PEDOT/PSS nanowire assembled into position using dielectrophoresis. The devices typically had a linear current-voltage (I-V) characteristic.

In order to extract $\sigma$, the electrical conductivity of the polymer, and the device contact resistance $R_0$, the resistances of 14 samples with varying diameter and length of
the polymer region were measured. With the assumption that the contact resistance $R_0$ is constant for each sample, the sample resistance $R$ is expected to be:

$$R = R_0 + \frac{1}{\sigma A} \frac{l}{A}$$  \hspace{1cm} (Eq. 2)

where $\sigma$ is the electrical conductivity of the PEDOT/PSS, $l$ the length of the polymer segment of the nanowire, and $A$ its cross-sectional area. The quantities $l$ and $A$ were measured using scanning electron microscopy (SEM) or atomic force microscopy (AFM).

We find that the polymer portion of the nanowire is typically 6 $\mu$m long and 220 nm in diameter, with a sample-to-sample variation of each of these parameters of 10%.

![Graph](image)

Figure 3-13 Current-voltage characteristic of a single polymer nanowire. Inset: Sample following dielectrophoretic assembly.

Fig. 3-14 shows a plot of $R$ vs. $l/A$ for 14 samples, demonstrating that these quantities are linearly correlated as expected. A contact resistance between PEDOT/PSS and gold of $R_0 = 27.6 \pm 4$ K$\Omega$, and a conductivity of the PEDOT/PSS $\sigma = 11.5 \pm 0.7$ S/cm is extracted from a fit of the experimental data to Eq. 2. This latter value is comparable to earlier
reports of the conductivities of thin films of similar polymers\textsuperscript{35,91}, which ranged from 0.03 to 80 S/cm, depending on the PEDOT:PSS ratio.

\[ R_c = 27.6 \pm 4 \, \text{k}\Omega \]
\[ \sigma = 11.5 \pm 0.7 \, \text{S/cm} \]

Figure 3-14 Resistance v.s. length/(cross-sectional area) \( l/A \) is plotted for 14 samples.

3.4 Gas-sensing properties

Figure 3-15 (a) Gas delivery system; (b) a schematic describing how this system controls the concentration of analytes; (c) A small chamber inside the big steel box which is used for noise-shielding.
Measurements of the gas-sensing properties of nanowire devices were conducted under ambient conditions using a homebuilt apparatus, shown in Fig.3-15a. The system can be divided into three parts: gas delivery, electronic measurement and DC heating subsystems. The diagram of gas delivery subsystem is shown in Fig.3-15b. Mass flow controllers regulated the flow of nitrogen (99.999% purity) carrier gas through two lines. One line was bubbled through the liquid analyte, providing a known flow rate of a saturated vapor. Saturated vapors ($P_0$) of the analytes used here are, in parts per thousand. The second nitrogen line was mixed with the flow of saturated vapor to bring the total gas flow to a standard level (typically 1000 sccm). By controlling the relative flow of the two lines, vapor of known analyte concentration ($P/P_0$) was created and then delivered to the sample which was confined onto the small chamber in Fig.3-15c by mounting the sample upside down over the opening with an o-ring sealing the interface. A DC heater was mounted on top of the sample substrate to control the temperature. Pure nitrogen was used to flush the sample chamber by switching the two-way solenoid valve. To reduce electrical noise, the whole sample was concealed in a big steel box.

3.4.1 Titanium oxide nanowire sensors

Due to extrinsic impurity, the TiO$_2$ nanowire we synthesized were likely p-type. The oxygen vacancy near the grain boundary at elevated temperatures formed a potential barrier for charge carriers (holes). When such a TiO$_2$ nanowire contacted by Pt/Cr electrodes (Fig.3-16a) was exposed to 20% O$_2$ at elevated temperatures, ionized O atoms
were adsorbed onto the grain boundaries, which reduced the potential barrier and increased the conductivity (Fig.3-16c). In this case, we observed the current increased on exposure to O$_2$ and decreased when O$_2$ was flushed away by N$_2$ (Fig.3-16b,d).

An elevated temperature is an important favorable factor for ionizing O$_2$. In the experiments, we didn’t observe any visible change in the nanowire resistance when exposed to O$_2$ at a temperature lower than 150C. However, this does not mean extremely high temperatures are always favorable to the sensitivity since the sensitivity is also affected by the internal conditions of the nanowire itself. At extremely high temperatures, charge carriers can be readily activated to an energy level much higher than the potential barrier between the boundaries. In this case, the same amount of decrease in potential

Figure 3-16 (a) A single TiO$_2$ nanowire; (b) Current change over time when the wire is exposed to 20% O$_2$ at 215C; (c) The potential barrier between two TiO$_2$ grains is reduced by exposure to O$_2$; (d) Current change over time when the wire is exposed to 20% O$_2$ at 250C.

An elevated temperature is an important favorable factor for ionizing O$_2$. In the experiments, we didn’t observe any visible change in the nanowire resistance when exposed to O$_2$ at a temperature lower than 150C. However, this does not mean extremely high temperatures are always favorable to the sensitivity since the sensitivity is also affected by the internal conditions of the nanowire itself. At extremely high temperatures, charge carriers can be readily activated to an energy level much higher than the potential barrier between the boundaries. In this case, the same amount of decrease in potential
barrier induced by O\textsuperscript{−} is only favorable to those low energy carriers (holes here) and thus has much less effects on the overall conductance of the wire. As observed in many other metal oxide nanowire sensors\textsuperscript{92}, there is an optimal temperature that maximizes the sensitivity. This optimal temperature for TiO\textsubscript{2} sensors is located in a range between 400\textdegree C and 600\textdegree C. The temperature at the engine exhaust is also in this range. For this reason, TiO\textsubscript{2} sensors have been widely used to monitor the performance of engines\textsuperscript{93} by detecting O\textsubscript{2} in the exhaust.

Nanowires have a higher surface-to-volume ratio than thin films, which allows analytes to diffuse into the bulk more easily. As we expected, the “real-time” response in Fig.3-16b and d indicates that the nanowire responds much more rapidly (~50s) than thin film sensors (~10 minutes)\textsuperscript{90}. In the recent years, researchers have reached a consensus that the sensitivity of metal oxide nanowire sensors is significantly improved over thin film sensors only when their diameter is smaller than 25nm.\textsuperscript{94} The possible reason is that the depletion depth (Debye length) is comparable to this “magic” number (~12nm, half of this number). Our nanowires have a much larger size (~150nm) so that only a very thin exterior shell (~12nm) is affected by the analytes. For this reason, we only observed a similar sensitivity compared to thin films sensors.

3.4.2 Conducting polymer nanowire sensors

We exposed single nanowire sensors assembled by dielectrophoresis (Fig.3-2a) to methanol, ethanol and acetone vapor of various concentrations. Typical sensor response
data are plotted in Fig.3-17a. The nanowire shows rapid (~30s), reversible responses to all three analytes, and rapid recovery to baseline when exposed to air. Sensor response (\(\Delta R/R\)) as a function of analyte concentration \(c\) (Fig.3-17b) shows a power-law variation:

\[
\Delta R / R = A c^\beta \quad \text{(Eq.3)}
\]

The exponent \(\beta\) is found to increase with the molecular weight of the analyte: the values of \(\beta\) are 0.69, 0.73, 0.80 for methanol, ethanol and acetone, respectively. We defined a minimum detectable concentration for a single device based on the noise floor (\(\Delta R / R \sim 0.1\%\)), which was intrinsic to the nanowires. The detection limit was found to be approximately 0.06\% (76ppm), 0.14\% (110ppm), and 0.5\% (1200ppm) of a saturated vapor for methanol, ethanol and acetone vapor, respectively. The electrical response of the nanowire sensor is approximately 10 times faster than that reported for PEDOT/PSS film sensors, with comparable sensitivity. Additional experiments are required to
determine whether smaller diameter devices offer further improvements over the thin film counterparts.

As it was commonly observed in other conducting polymers, the conductance of our nanowires increases as the temperature rises (data not shown here), which indicates the PEDOT/PSS is semiconductive. Thus the electrical resistance of the nanowire should follow the semiconductor relation

\[ R = R_0 \exp(\frac{E_a}{kT}) \]

where \( R_0 \) is temperature-independent, \( k \) is the Boltzmann’s constant and \( E_a \) is the thermal activation energy. The activation energy can be roughly estimated to be \( E_a \approx 23\text{meV} \), a relatively small value.

When used as a sensor at elevated temperatures, the nanowire response to analytes still follows a power law as Eq.(3) in which the sensitivity \( A \) decreases as the temperature rises (Fig.3-18), leading to a lower detection limit of ethanol vapor at 40°C and 60°C.
This degraded sensing behavior is due to the enhanced degassing effect at elevated temperatures. Very few papers clearly interpreted the physical implication of $\beta$ which, in the case of ethanol vapor, increases from 0.73 at room temperature to 0.82 at 40°C and 1.28 at 60°C (Figure 3-18b). We believe $\beta$ represents the spatial distribution characteristic of transduced resistivity, which is interpreted in details as following.

![Diagram](image)

Figure 3-19 (a) Microscopic view of a nanowire cross-section. Analyte molecules are adsorbed in a thin layer near the surface (origin) which will transduce a depletion region extended into the bulk (blue); (b) The nanowire sensor is exposed to analytes with different mobility. Analyte with a higher mobility will diffuse deeper from the surface which will extend the transduced carrier depletion region further into the bulk; (c) In semiconductive nanowires, more carriers will be available at elevated temperatures which push back the depletion region.

When the nanowire sensor is exposed to analyte, the analyte molecules will be adsorbed in a thin layer near the surface (Fig.3-19a) with their concentration decay from the surface as the red curves indicate in Fig.3-19b and c. The interaction of the analyte molecules with the polymer chains will transduce a depletion region of carriers
(resistance increases in our case) as the blue curves. The sensitivity constant $A$ in Equ.(2) is the transduced amplitude while the exponent $\beta$ is proportional to the slope of the blue curves near the surface, shown in Fig.3-19b and c. If the concentration of adsorbed molecules exponentially decays from the surface, the “strength” of the carrier depletion will follow some specific function (a known implicit function). Therefore using the constant $A$ and $\beta$ near the surface can incorporate all macroscopic information of the sensing process that is determined by properties of the analyte and the sensor material.

In Fig.3-19b, if the sensor is exposed to an analyte that has a higher mobility (other parameters are assumed to be the same), the distribution of the adsorbed analyte will extend further from the surface which pushes the depletion region deeper into the bulk as the arrow indicates. Then the exponent $\beta$ will decrease to a smaller value. This is consistent with what we observed in Fig.3-17b. For methanol (one carbon), ethanol (two carbons) and acetone (three carbons), their mobility decreases sequentially. We observed the exponent $\beta$ for these three analytes increased in sequence as the proposed theory predicts.

Semiconductors at elevated temperatures have a higher carrier concentration that narrows down the depletion region, as the arrow indicates in Fig.3-19c. As a result, the slope of the blue curve increases, leading to a greater value of $\beta$. In Fig.3-18b we observed the exact same phenomenon: when the temperature is elevated from 20°C to 40°C and 60°C, the power-law exponent increases from 0.73 to 0.82 and 1.28, respectively. However, elevated temperatures also increases the mobility of molecules
which will extend the molecule distribution further into the bulk and scale down the value of \( \beta \). The reason that we still observed an increased value of \( \beta \) is because the former phenomenon dominated this competition due to a very small thermal activation energy \( \sim 23 \text{meV} \) of our PEDOT/PSS nanowire sensors.

![Graph showing relative resistance over time](image)

Figure 3-20 (a) Five nanowire devices show similar response to methanol exposure, with the exception of sample R2, which shows a clearly smaller response; (b) one of the cycles is enlarged. All nanowires reach 90% of their final value within 30s in the response phase and \( \sim 40 \text{s} \) during recovery phase.

In order to investigate the repeatability over samples, we characterized the response of multiple nanowires simultaneously. To do this, a solid state multiplexer (MAXIM DG406DJ) was used to switch electrical connections from nanowire to nanowire every 100ms. Fig.3-20a shows the relative resistance \( R/R_0 \) (where \( R_0 \) is the nominal nanowire resistance measured in a flow of pure nitrogen) of five nanowires (R1 to R5) upon exposure to 20% saturated vapor of methanol. The nominal resistances \( R_0 \) of the 5 nanowires in pure nitrogen were 43.8k\( \Omega \), 32.8k\( \Omega \), 45.5k\( \Omega \), 42.2k\( \Omega \), and 48.4k\( \Omega \), respectively. Four of the nanowires showed similar responses of \( +2.2 \pm 0.3 \% \), while the
fifth (R2) has a response of 1.5%. This observation of small sample-to-sample variation in wire resistance and gas sensing response is typical of more than 40 nanowire devices that have since been characterized. Because of its strong difference from the other nanowire devices, sample R2 was not included in measurements of the average gas sensing response presented below. Response and recovery to methanol exposure occurred within 20-40 seconds (Fig.3-20b).

Summary

In this chapter, we synthesized \( \text{TiO}_2 \) and "striped" conducting polymer nanowires using electrochemical-templating method. Single \( \text{TiO}_2 \) nanowires were made contact using electron beam lithography and single conducting polymer nanowires were electrically connected after dielectrophoretically assembled onto a pair of gold electrodes. Electronic and gas-sensing properties at elevated temperatures were characterized for both types of nanowires. Their conduction and sensing mechanisms were explained.
Chapter 4
Integration of Heterogeneous Nanowire Sensors

Conducting polymer and metal oxide nanowire sensors have been synthesized and characterized in Chapter 3, which has laid a solid foundation for heterogeneous integration of these nanowire sensors. In this chapter, we first analyze challenges for development of electronic nose systems and then review current technological progress that has a potential to address these challenges. As the most important part of this chapter, a novel on-chip electrochemical templating approach is proposed to provide a full solution for all these challenges. This chapter continues to demonstrate the proposed idea by fabricating the on-chip nanochannel template and integrating Ag, Au, Sn and TiO₂ two terminal and multiterminal nanowires. At the end of this chapter, integration of CMOS circuits with heterogeneous nanowire arrays is designed and the microhotplate technology is proposed to solve the operation temperature incompatibility of CMOS circuits and nanowire sensors.

4.1 Challenges for the development of electronic noses

The development of a low footprint artificial smart “electronic nose” (E-Nose) will open a wide range of applications such as clinical assaying, emission control, explosive detection, agricultural storage and shipping, and workplace hazard monitoring. However,
despite several decades of intensive research, the goal of creating such an E-Nose that can compete with a biological olfactory system has yet to be achieved.\(^1\)

![Diagram of olfaction system and electronic nose system]

Figure 4-1 (a) the olfaction system of human beings can be divided into three parts: pattern classifier, sensor array and sampling system. (b) Correspondingly the electronic nose system can also divided into three parts. The part that has hindered the development of an electronic nose is the sensor array part. The figures are from http://electrochem.cwru.edu/ed/encycl/fig/n01/n01-f01b.jpg

The difficulties to make such sophisticated E-Noses lie in the several aspects. First is the extremely large chemical diversity and massive parallelism that is characteristic of mammalian olfactory systems. For example, the human nose has more than 400 different types of sensory cells and each type is replicated over 100,000 times, for a total of over 40 million cells overall (Fig.4-1a).\(^2\) The microelectronic technology faces a huge obstacle...
to make such a sensor array in terms of the scale and chemical diversity (Fig.4-1b).

Figure 4-2 The biological structure of the olfaction. Different types of olfactory cells are spatially spread in a wide range. (http://www.life.uiuc.edu/hing/)

A second important factor is that heterogeneous sensory cells are widely distributed in the whole sampling system (the nose nostril for human nose), as shown in Fig.4-2. Otherwise, signals from some analyte molecules may not be picked up by a specific type of sensors if they are highly localized in one region. This diversified physical distribution poses a huge difficulty for fabrication.

Thirdly, microscale chemical sensors typically respond slower, are less sensitive than their counterparts in biological olfactory systems. For example, human noses can detect analytes as low as tens of ppb in less than a second that microsensors usually cannot. In addition, it is widely known that biological olfactory systems may generate false alarm in some specific cases. One way for E-noses to improve performance in this aspect is to
design multiterminal sensors such as Tetrapod sensors that were recently demonstrated, shown in Fig.4-3. However, integrating these multiterminal sensors will be another big challenge.

To build a smart and sophisticated electronic olfaction system, we need to integrate all these features mentioned above.

Figure 4-3 (a) An SEM image of a three terminal sub-micro sized sensor. (b) The diagram of this sensor in a circuitry. (from ref. 98)

4.2 Current Technological Development

Recent development in nanotechnology has offered some solutions for the aforementioned challenges we face. For example, the sensitivity of nanowires with a diameter smaller than 25nm is highly enhanced compared to thin film sensors. In$_2$O$_3$
nanowires with 10 nm diameter, synthesized using the VLS method, had a sensitivity 4-5 orders of magnitude better than that of thin film sensors of the same material. Exposure to 5ppb NO\textsubscript{2} at room temperature induced a 20% change in conductance, although this response was rather slow, requiring 1000s as shown in Fig.4-4b. It was also reported elsewhere chemiresistive V\textsubscript{2}O\textsubscript{5} nanowires/fibers several micrometers long and \~10nm in diameter could detect some analytes at a level of 30 ppb (Fig.4-4c and d). To a certain degree, these developments in nanotechnology can satisfy the high sensitivity requirement of a sophisticated E-nose system.

Figure 4-4 (a) Single In\textsubscript{2}O\textsubscript{3} nanowires contacted by Ti/Au electrodes; (b) the In\textsubscript{2}O\textsubscript{3} nanowire sensors can detect NO\textsubscript{2} analyte as low as 5ppb; (from ref. 44) (c) V\textsubscript{2}O\textsubscript{5} nanowires several micrometers long and \~10nm in diameter; (d) V\textsubscript{2}O\textsubscript{5} nanowire sensors can respond to 30ppb 1-butylamine. (from ref. 48)

Advance lithography technologies such as deep UV photolithography, E-beam lithography (EBL) and nanoimprint lithography (NIL) have been able to make
nano devices. Due to their controllability and flexibility, it is quite reasonable to use these technologies to make large arrays of nanoscale sensors. It was reported that nanoimprint lithography was employed to create dense arrays of silicon nanowires over a large area (Fig.4-5a). More recently, a titanium oxide polycrystalline nanowire array for gas sensing applications was also reported. In this report, a solid thin film of titania was first deposited using the sol-gel technique and the film was then patterned into an array of nanowires by the side etching effect of SF6 plasma after photolithography, shown in Fig.4-5b. These technologies are perfect for fabrication of a single type of nanowires. However, integrating more types of nanowires will result in incompatibility with standard IC processes and significantly increase the fabrication steps, leading to extremely high cost and low yield.

Figure 4-5 (a) Silicon nanowires made by nano imprinting (from ref. 105). (b) TiO2 nanowires made by photolithography (from ref. 106).

To our best knowledge, Langmuir-Blodgett (LB) assembly-transfer technique is the most promising technology to integrate nanowires arrays so far. The technique starts with turning free-standing nanowire suspension into hydrophobic by coating them with a surfactant. The assembly process is a microscopic version of “log-on-a-river”. Randomly
oriented nanowires on the surface at zero pressure will start to align to the LB trough barrier at some critical pressure (Fig.4-6). However, nanowires assembled using this technique have 5-10 degree of misalignment (right figures in Fig.4-6). It is therefore difficult to make single-nanowire devices. It has been demonstrated that each type of nanowires can be assembled in separate individual groups using LB technique. This technique, however, has very limited choices to assemble different types of nanowires in a pattern other than one type in one group. The “front end” of an E-nose system requires a sensor array with a wide spatial distribution of heterogeneous nanowires, which is a serious challenge for the LB technique. More important, multiterminal nanowires will not be able to align in parallel. The LB technique is unable to assemble multiterminal nanowires that, however, are superior to two terminal nanowire sensors in terms of reliability.\textsuperscript{98}

![Figure 4-6](image)

Figure 4-6 Left-top: Hydrophobic nanowires are randomly distributed on the surface at zero surface; Left-center: compressed nanowires are remarkably aligned in parallel at some critical pressure; Left-bottom: different types of nanowires are grouped together at different locations; The right figures are the SEM images of aligned nanowires. The scale bar is 100\textmu m. (from ref. \textsuperscript{107})
4.3 A novel proposal

Figure 4-7 (a) A nanochannel template with each channel connecting to its own electrode. (b) Two types of nanowires can be synthesized right next to each other. (c) Two types of nanowires are synthesized. The same type of nanowires is grouped together. (d) Two terminal and three terminal nanowires can be synthesized on the same chip by properly designing the template.

In order to overcome these difficulties, here we propose a new approach to integrate heterogeneous bi-terminal and multiterminal nanowire sensors for E-Nose applications, shown in Fig.4-7. The approach starts with an on-chip nanochannel template with each horizontal channel connected to a platinum electrode (Fig.4-7a). Nanowires are grown inside the template by electrochemical deposition. This design allows for addressable synthesis of a specific type of nanowires in specified channels by providing a voltage to the electrodes connecting to those channels. The process can be further repeated to
produce different types of nanowires in other channels using different electroplating solutions. The heterogeneous nanowires can be physically distributed in any designed pattern, for example, different types right next to each other (Fig.4-7b) or the same type in one group (Fig.4-7c). In addition, a proper design of the nanochannel template can integrate multi-terminal nanowires on the same chip in a designed pattern, shown in Fig.4-7d.

As it is known, a wide range of sensor materials have been made into nanowires by electrochemical deposition using anodic aluminum oxide (AAO) membrane templates, including metal oxides\textsuperscript{77}, compound semiconductors\textsuperscript{57} and conducting polymers\textsuperscript{18, 108}, such as TiO\textsubscript{2}, SnO\textsubscript{2}, ZnO WO\textsubscript{3}, PEDOT/PSS and poly-aniline, etc. However, nanowires grown inside the nanopores are standing vertically on the substrate surface and hard to make contacts. The on-chip templating concept demonstrated in Fig.4-7 can avoid this difficulty and offer us the same capability of synthesizing different materials as we use AAO membrane templates.

In brief, using this on-chip template method, a high-density, large-scale heterogeneous bi-terminal and multiterminal nanowire sensor arrays can be integrated on-chip in any designed pattern. This method is a promising approach to address all the aforementioned challenges for the development of an E-nose system.

4.4 On-chip Template Fabrication
Figure 4-8 (a) An array of PMMA nanoribbons are fabricated with each connecting to its own electrode. (b) A thin film, ideally Al₂O₃ or SiO₂ is covered the surface of the chip in (a). The thin film is then patterned so that PMMA nanoribbon is open to air.

The critical step to realize the concept in Section 4.3 is to fabricate the on-chip nanochannel template with each channel connecting to its own electrode. It can start with fabrication of an array of PMMA nanoribbons (green bars in Fig.4-8a) with each connecting to a prefabricated gold electrode. The whole surface is then covered with a dielectric layer such as SiO₂ or Al₂O₃ which is patterned thereafter as shown in Fig.4-8b. A nanochannel template with each channel connecting to its own electrode will be formed after the PMMA nanoribbons are removed.

Many options are available to fabricate the nanoribbon array. Nanoimprint Lithography (NIL) is one of the best options in terms of industrial applications. Fig.4-9a demonstrates the concept of NIL which employs a hard template press against PMMA at its glass transit temperature (~105°C).¹⁰⁹ High quality nanoribbon (~100nm) arrays were fabricated using NIL as shown in Fig.4-9b. We made relatively large-sized (~500nm) nanoribbon arrays using the same method in the lab (Fig.4-9c). Indeed, to demonstrate the E-nose concept based on nanowire sensors in the lab does not require a large-scale
nanowire array at an industrial level. Employing NIL to develop an E-nose primitive model is premature. We therefore choose to use electron beam lithography to make this nanoribbon array (Fig.4-9d, several hundred nanoribbons).

Figure 4-9 (a) the process of Nanoimprint (from ref.\textsuperscript{110}); (b) 100nm wide nanoribbon arrays fabricated using NIL in the literature (from ref.\textsuperscript{111}); (c) 500nm wide nanoribbon arrays fabricated in our lab. The SEM image is courteous of Yongan Xu. (d) PMMA nanoribbons fabricated using EBL.

The intensity of the Ebeam in EBL follows a Gaussian distribution over space.\textsuperscript{112} When two electron beams are close to each other, the resist between them that is supposed to be unexposed will be partially exposed. The partially exposed resist is unable to be well defined after development. This is the so-called "proximity" effect\textsuperscript{112} which limits the unexposed PMMA nanoribbons above some size, for example 200nm in width as we found in experiment (probe current 30pA at a dose of 500\mu C/cm\textsuperscript{2}). It is a big challenge to fabricate nanoribbons narrower than 100nm on positive ebeam resist PMMA using this method.
Figure 4-10 (1) PMMA exposed to a proper dose of Ebeam will be developed. (2) Over-exposed PMMA will not be dissolved by developers.

However, due to the flexibility of EBL, we still prefer using EBL to fabricate PMMA nanoribbons near or below 100nm in width. As it was demonstrated years ago\textsuperscript{113}, we find another approach to fabricate PMMA nanoribbons below 100nm in width using EBL as shown in Fig.4-10. On exposure to high energy electron beams, polymer PMMA will be depolymerized into segments that will be dissolved by the standard developer (MIBK:IPA=1:3), shown in Fig.4-10(1). The depolymerized segments will be polymerized again upon further over-exposure to ebeam (20-30 times higher dose) as shown in Fig.4-10(2). Fig.4-11 shows the over-exposed nanoribbons 20nm in height and 50nm wide with each connecting to its own electrodes.

To fabricate a template, a layer of SiC\textsubscript{2} was deposited on the nanoribbon surface and the whole sample was then baked at 500C in air for 30min. The over-exposed PMMA nanoribbons were decomposed into gaseous residue and hollow channels were formed underneath the deposited SiO\textsubscript{2} layer. CF\textsubscript{4} plasma was employed to etch one end of the channels to open to air, schematically shown Fig.4-12a. An SEM image of these channel...
openings is shown in Fig.4-12b.

Figure 4-11 (a) a top view and (b) a side view of overexposed PMMA nanoribbons with each connecting to its own electrode.

Figure 4-12 (a) A schematic of nanochannels open to air (b) SEM image of nanochannels open to air. The bar is 1μm.

Figure 4-13 shows the gold nanowire array after the top SiO₂ layer is etched away by CF₄ plasma. These gold nanowires are approximately 100nm in diameter (Fig.4-13b) and 8 –10μm long. The existence of these gold nanowires is direct evidence that the nanochannels are continuous inside. The non-uniformity of the nanowire length is likely caused by the diameter variation of the nanochannels that affects the nanowire growth rate by limiting the electrolyte diffusion along the channel.

In order to test whether the nanochannels fabricated using this method were continuous inside or not, we deposited gold into these nanochannels by electrochemistry.
Figure 4-13 (a) SEM image of gold nanowire arrays. The nanowires are 8-10µm long and ~100nm in diameter as shown in (b).

Figure 4-14 (a) An array of electrodes fabricated on 1”×1” Si/SiO₂ substrate. (b) Each of these electrodes running from the substrate edge splits into ten of 500nm electrodes in the center of the substrate. (c) A schematic showing PMMA nanoribbons with each connecting to its own electrode. (d) AFM image of such a nanoribbon array, schematically shown in (c).

We fabricated tens of microelectrode pads on the edge of the 1”×1” wafer for wire-bonding (Fig.4-14a). Each electrode was running from the edge to the center where
it split into tens of 500nm wide electrodes (Fig.4-14b). EBL was employed to fabricate PMMA nanoribbons with each connecting its own electrode, schematically shown Fig.4-14c. Fig.4-14d shows the AFM image of PMMA nanoribbons 200nm wide, 100nm high and tens of micrometers long.

4.5 Heterogeneous Integration

A bottomless container was placed on the template which is schematically shown in Fig.4-15b and the space between them is sealed by an o-ring (Fig.4-15a). One electrode pad is wire-bonded each time. The electrolyte, counter electrode and reference electrode are placed inside the container as shown in Fig.3-1b. Nanowires will grow inside the nanochannels that electrically connect to the electrode pad (working electrode). Disconnect the working electrode and wire-bond to a different electrode pad. Replace the electrolyte with a different one after the container is rinsed with DI water. A different type of nanowires will grow inside different nanochannels that are electrically connecting to the new electrode pad. Different types of nanowires can be synthesized in any designed location by repeating this process multiple times.

Fig. 4-16a shows an optical image of silver, gold and tin nanowires are integrated on the same chip using the approach described above. This figure has proven the concept proposed in Section 4.3 is practical. Properly design the template and we can grow two-terminal, three terminal and five terminal nanowires as shown Fig.4-16b. These nanowires are titanium oxide whose synthesis is described in details in Chapter 2. EDX
spectrum is employed to analyze titanium oxide on Si/SiO₂ substrate as shown Fig. 4-16c. For electronic nose application, different types of nanowires, for example, conducting polymers PEDOT/PSS and metal oxide TiO₂, SnO₂, ZnO need to be integrated together. Currently we have not integrated these nanowire sensors on chip. More work on this goal needs to be done.

Figure 4-15 (a) an optical image of a bottomless container on the template substrate. (b) A schematic showing the template in (a).

4.6 Challenges for the Development of a CMOS compatible E-nose chip

A smart E-nose system requires an extremely large number (10³-10⁷, for example) of single nanowire sensors. Integration of these nanowires with on-chip multiplexers and other circuitry for signal processing is a must to electrically monitor these nanowire sensors individually. To demonstrate the concept of E-nose, an on-chip multiplexer system with 10 thousand signal channels can be designed and fabricated by a commercial foundry (Fig.4-17). Each of these signal channels has an electrode that is lined up with a PMMA nanoribbon fabricated by EBL or NIL. A layer of aluminum oxide thin film is then sputtered to cover the surface and then patterned afterwards using Cl₂/BCl₃ dry etch process. The PMMA nanoribbons are then removed by rinsing the whole chip in acetone,
after which a nanochannel template with each channel connecting to its own electrode is therefore formed. Fourteen electrode pads on the edge can access these 10 thousand channels individually. After different types of nanowires are synthesized in the channels, the whole chip can be rinsed in NaOH to dissolve Al₂O₃ and expose the nanowires for sensing application.

Figure 4-16. (a) Optical image of Ag, Au and Sn nanowires synthesized in the on-chip template. (b) AFM image of two-terminal, three-terminal and five-terminal TiO₂ nanowires integrated together. (c) EDX spectrum shows Ti signal in the nanowire array.

In order to increase the chemical diversity of the sensor array, hopefully 10+ kinds of nanowires can be integrated on-chip, for example, conducting polymer nanowires (such as PEDOT/PSS, Polyaniline) and metal oxide nanowires (TiO₂, ZnO and SnO₂, …) including their doped counterparts.

However, as it’s known, CMOS circuits fabricated by standard CMOS technology cannot operate at a temperature higher than ~100C while those fabricated by the
silicon-on-insulator (SOI) CMOS technology have a potential of operating at 250°C.\textsuperscript{114} Some metal oxide sensors have to work at an a temperature up to 400°C-600°C to reach its optimal performance.\textsuperscript{93} The data from Chapter 3 shows conducting polymer sensors are sensitive to vapors at room temperature and the sensitivity is significantly reduced at elevated temperatures. One major reason that a sophisticated E-nose system has not been achieved yet after decades of development is likely because of this temperature incompatibility of CMOS circuits and different types of sensors.

Figure 4-17 A schematic layout of an integrated multiplexer array that controls around 500 electrodes.

In recent years scientists at National Institute of Standard Technology (NIST) have developed the microhotplate technology that can locally control temperatures at a micrometer scale.\textsuperscript{115,116} The microhotplate is fabricated on a suspended Si\textsubscript{3}N\textsubscript{4} membrane and poly-silicon is used as power lines for the hotplate. Heat is isolated from the silicon
substrate and concentrated near the center of the membrane where the temperature can go up to 400°C while keeping the temperature of the substrate below 100°C. This technology provides a reasonable solution for integrating heterogeneous sensors with CMOS circuits.

Figure 4-18 An array of Microhotplates integrated on-chip (from ref 116).

Summary

A sophisticated E-nose system has features of i) a large sensor array, ii) massive chemical diversity, iii) highly sensitive sensors, iv) wide spatial distribution, and v) multiple-terminal sensors. Current technologies cannot offer a solution that can integrate a sensor array with all these features. In this chapter, we proposed and demonstrated a novel on-chip electrochemical-templating approach that can integrate such as a sensor array. The incompatibility of operating temperatures of heterogeneous
nanowires and CMOS circuits may be the major hurdle that hindered the development of a sophisticated E-nose system. A well-developed microhotplate system is proposed to circumvent this difficulty at the end of this chapter.
In this chapter, we move to a new field that is independent of the work on electronic noses in previous chapters: exploring the properties of graphene, a single layer of graphite first exfoliated from bulk graphite in 2004. In this chapter we first briefly introduce the history and properties of graphene and then describe the mechanical exfoliation of few-layer graphene films. The fabrication of graphene devices using electron beam lithography will be discussed in Section 5.3, followed by a discussion of device measurements in Section 5.4. Section 5.5 is from a submitted manuscript, where we describe experiments that reveal the intrinsic vapor sensor responses of graphene field effect transistors.

5.1 Introduction to Graphene

3-D graphite, 1-D carbon nanotube and 0-D bulky ball each attracted extensive attention due to new physics arising from their unique structures. After the discovery of nanotubes in 1991, 2-D graphene was the only “missing member” of this family, and was believed by many to be thermally unstable and therefore not realizable. This all changed when single layer graphene was isolated from bulk graphite in 2004 using mechanical exfoliation. Indeed, the mechanical exfoliation method can only isolate micro-sized graphene sheets hidden in thousands of thick graphite flacks. However, it is
almost impossible to locate such small sized graphene sheets using modern techniques such as atomic force microscopy (AFM) in an area as large as 1 cm$^2$. The trick leading to discovery of graphene in 2004 is that single layer graphene sheets on the silicon substrate with 300 nm thick SiO$_2$ are visible under an optical microscope$^{121}$ (Fig. 5-1a, b). The faint contrast of graphene in an optical microscope can even be used to estimate the number of layers of graphene. The optical microscope allows us to scan a very wide region and locate few-layer graphene sheets. AFM is then employed to verify the layer number of graphene sheets, $N = t/d$, where $t$ is the measured thickness of the graphene sample, and $d = 0.34$ nm is the graphite layer spacing. Fig. 5-1c shows an AFM image of several stripes of single-layer graphene sheets.

Figure 5-1 Single layer graphene sheets are visible under optical microscope. (a) Graphene sheets under microscope at a low magnification. (b) A close view of graphene sheets. (c) AFM image of graphene sheets located by optical microscope. The height scale bar is 10 nm.

Theory predicts that a strict 2-D single layer graphene is thermally unstable$^{119, 120}$, which seems in contradiction to the exfoliation of a single layer graphene from bulk graphite. Recent discovery$^{122}$ that a single layer graphene has ripples in the third
dimension (Fig.5-2) has unified the theories and experimental discovery together.

Figure 5-2 Ripples exist in the third dimension of freestanding graphenes. This figure is from Ref. 122.

Due to its 2D honeycomb structure, graphene has a zero-bandgap cone-shaped band structure (Fig.5-3 a, b). This unique structure leads to a Dirac behavior of charge carriers in graphene, i.e. like massless Dirac particles\(^\text{123}\) (photons, for instance), the energy of charge carriers in graphene follows the equation \(E=h\times v=h\times v_F\times k\), where \(v_F\) is Fermi velocity. To illustrate the properties of graphene devices as transistors, a single layer graphene sheet contacted by a pair of gold microelectrodes on an oxidized \(p^{++}\) Si substrate (the back gate) is sketched in Fig.5-3c. Sweeping the gate from negative to positive corresponds to moving the Fermi energy from the valence band to the conduction band (Fig.5-3d). The conductivity of the graphene thus follows a “V” shape and reaches its minimum when the Fermi level is at the crossing point of the valence and conductance band, also known as the charge neutrality point. Thermally activated charge carriers (electrons and holes) and inhomogeneity in the charge density of the sample lead to rounding of the “V” when the Fermi energy level is close to the band crossing at
Graphene may be thought of as a zero bandgap semiconductor and it exhibits ambipolar behavior in current vs. gate voltage (IVG) curves and a small ON-OFF ratio (several or tens) in a wide range of gate voltage (tens of volts). This seriously limits its applications in many aspects, in particular digital electronics. An important research topic, therefore, is to develop methods to induce a larger band gap in the material. These techniques include cutting graphene into nanoribbons\textsuperscript{125} and generating a potential difference between the two layers of a bilayer graphene\textsuperscript{126}. Luckily, the small ON-OFF ratio originated from zero band-gap does not preclude analog applications in high...
frequency circuits in which transistors are always working at some DC current offset. More important, graphene has an intrinsic mobility as high as 200,000 cm²/Vs at room temperature which exceeds the intrinsic mobility of any other known semiconductors. And unlike other semiconductors, this high mobility will not degrade at a high carrier concentration and can switch ON-OFF the transistor at a very high speed. With these properties, graphene transistors are therefore ideal candidates for applications in THz circuits.

The electric screening length in graphite is only 5Å, so graphene films with 4 or fewer carbon layers display properties that differ significantly from the bulk. In particular, molecules bound to the graphene surface may transfer charge to the graphene or to other molecules in the environment (e.g. water), and thereby chemically gate the graphene. For thin graphene samples (< 4 layer), this chemical gating effect will penetrate to the layer underneath and tune their electronic properties. Few-layer graphenes are thus excellent candidates for application as chemical vapor sensors. In section 5.5 we describe the results of first experiments done in the Johnson lab on graphene vapor sensors.

5.2 Preparation of Graphene Sheets

Different approaches have been tried to isolate a single layer of graphene for decades. Basically, these approaches can be divided into two categories. The first category is to deposit graphene by reducing silicon carbide thin films or epitaxy growth on transition
metals\textsuperscript{131}. Reducing silicon carbide will remove the silicon atoms and leave behind
graphitized carbons at a very high temperature (1600\textdegree{}C). However, graphene synthesized
in this approach has a very limited uniform size. The epitaxy growth on transition metals
can deposit large graphene sheets (tens of micrometers) in a large array. Its principle is
based on the temperature-dependent solubility of interstitial carbon in transition metals.
Carbons adsorbed at high temperatures in the metal will be driven out and crystallized on
the surface (ie. graphene sheets) when lowering the temperature.\textsuperscript{131}

The second category is to isolate graphene sheets from high quality graphite
chemically\textsuperscript{132} or mechanically\textsuperscript{117}. The chemical exfoliation approach is to intercalate
graphite (usually by acid) so that graphene planes become separated by layers of
intervening atoms or molecules (graphene is oxidized during this process). Mechanical
treatment (ultra sonication) is then employed to exfoliate the sheets of graphene oxide.
The as-prepared graphene oxide (GO) sheets are usually single layer or double layer,
water soluble, and highly resistive. In order to improve its electronic properties, the
graphene oxide is then reduced in a reducing environment.

The mechanical exfoliation method\textsuperscript{117} is the most popular approach among physicists
hoping to study the electronic properties of defect-free graphene. It can produce
single-layer or few-layer graphene sheets sparsely and random located on the substrate.
These graphene sheets usually have a size of tens or even hundreds of micrometers and
have been widely used in worldwide research labs.
Figure 5-4 (1) The tape was pressed against the bulk graphite. (2) When pulled away, a thin layer of graphite was left on it. (3,4) By folding the tape over and pressing it against itself, the graphite was spread over two areas of the tape. (5,6) By thinning the graphite further, it was made ready for deposition. This figure is courtesy of Nick Kybert.

As done in the Johnson lab, the mechanical exfoliation method involves taking a piece of scotch tape, pressing it against a piece of graphite, pulling it off, repeatedly folding the tape over and pulling it apart to thin the graphite on the tape and finally pressing the tape against the wafer to deposit graphite on the surface (see Fig.5-4). There are a few key factors to make large size high quality graphene sheets. The most important one is the quality of graphite. Generally “Kish” graphite (ordered from Covalent Materials Corporation) having very large crystal grains is the most favorable one. Graphene properly made out of “Kish” graphite can be as large as hundreds of micrometers. Graphene sheets exfoliated from SPI graphite (ordered from SPI Supplies) are quite small in most cases due to smaller crystal grains in the graphite. The second factor is how thick the graphite is after repeatedly folding the tape over. Films consisting of hundreds of layers of graphene will be very shiny, and when such a sample is pressed...
against a silicon substrate, it will leave thick graphite (more than 10 layers) and hardly leave few layer graphene. If the graphite on the tape is shiny, the tape should be continuously folded until the color of graphite become dull, shown as the step 3-6 in Fig.5-4.

After the tape has been sufficiently folded to give a large quantity of thin graphene flakes, the precise method used to press the graphite onto the substrate and then remove off the tape is also very important to make high quality graphenes. The most successful way is to use a rounded implement, such as a large marker pen, to rub back and forth across the chip very gently for an extended period of time (10mins for instance). The tape is then pulled off very slowly and at a very flat angle. These two factors together have the effect of increasing the density and enlarging the size of graphene left on the chip.

As mentioned above, graphene is visible using an optical microscope due to an interference effect with the 300nm layer of SiO₂. Specifically, the color of the graphene is related to the number of layers of graphene being viewed. While thick graphite chunks of more than 100 layers in thickness appear yellow in color, thinner multi-layer graphene appears blue and thin pieces of only a couple of layers in thickness are a faint purple. Single-layer graphene is even fainter, and must be carefully searched for, even with a high quality optical microscope.

5.3 Fabrication of graphene devices
Few-layer graphene sheets deposited by the mechanical exfoliation method are randomly located on the Si/SiO$_2$ wafer with prefabricated gold alignment markers. In order to make contact to graphene sheets, they must be located precisely with respect to prefabricated alignment markers. A standard approach to record the location is to take an SEM image at a magnification so that the target (the graphene sheet) and at least three (and ideally four) alignment markers are included in the image. In the software ELPHY Quantum, a precise pattern can be designed in a pattern design file after this SEM image is loaded into this file as a background (see Fig.5-5, Fig.5-6 and Fig.5-7).

However, taking an SEM image will deposit a very thin layer of carbon (contamination) which has a serious effect on the properties of graphene sheets. In order to avoid this problem, we choose a new approach that was not used widely in our lab before: we choose an optical microscope image instead of an SEM image.
This approach starts with a high quality digital optical microscope image at a magnification of 500. The image has a field of 160μm×160μm that covers four alignment markers and graphene sheets we are going to make contacts with. Open this image in
ELPHY Quantum as shown in Fig.5-5. Set the magnification to 500 and working area to 160μm×160μm. Open a new pattern design file in the edit mode. Choose "show video" in the Options menu (Fig.5-6). The optical image will show up in the pattern design file as a background. Measure the distances between alignment markers and make sure they are consistent with their real physical size (Fig.5-7). If not, properly scale up or scale down the canvas size of this image in Photoshop.

Place virtual alignment markers for electron beam writing on the center of each gold alignment markers and draw patterns of contact leads that will contact the graphene sheet (Fig.5-8). A close look of the contact leads is shown in the right part of Fig.5-8. The profile of a single layer of graphene is highlighted using white lines. Place the real sample in the SEM chamber and roughly align the sample by moving the right block (four alignment markers with the target graphene sheet inside) shown Fig.5-7 to the center of the screen at X500 and a working distance of 15mm. Use the standard alignment procedure to align the four gold alignment markers to the virtual alignment markers we just drew. After the virtual alignment markers are aligned to the real gold alignment markers, the pattern of contact leads we drew should be aligned to the graphene sheet as designed in Fig.5-8. Choose a proper dose (~500μC/cm² for PMMA on 300nm SiO₂) to expose the PMMA as the designed pattern. Develop the exposed PMMA in the standard developer (IBMK:IPA = 1:3) for 15s-45s. And then deposit 3nm of Chromium as an adhesion layer and 50nm of gold. In the end, the Au/Cr leads will be kept and rest part of Au/Cr thin film will be removed after liftoff process.
5.4 Extraction of carrier mobility in graphene

We characterized the electronic properties of the graphene device fabricated by the approach demonstrated in Section 5.3, schematically shown in Fig.5-3c. Since the extraction of graphene mobility from the I-Vg curve in Fig. 5-9 is a complicated procedure, we illustrate it here before moving to discussing the electronic and gas-sensing properties of graphene devices.

Mobility, one of the most important parameters for semiconducting devices, represents the speed of carriers moving in the devices driven by a unit of electric field, i.e., $\mu = v/E$, where $v$ is the carrier velocity and $E$ the electric field. The total current in the device is given by $I = Ne\mu$, where $N$, the number of carriers. The amount of charge carriers moving at this speed is equal to a specific amount of current flowing through the device. Tuning the amount of charge carriers will change the value of current. The
mobility of charge carriers can be extracted from this relation between charge carriers and current. Our graphene devices are placed on the Si/SiO₂ substrate, shown Fig.5-3c. The charge carrier and thus the current (Fig.5-9) can be tuned through the p⁺⁺ Si back gate by shifting the Fermi energy from valence band into conduction band.

![Figure 5-9 Current I vs. Vₜ of a bilayer graphene device 1μm long and 1.8μm wide at a constant bias voltage 1mV](image)

To extract mobility of graphene, we can take graphene as a 3-D or 2-D system, both of which lead to the same result eventually. Here we demonstrate these two approaches separately.

1) 3-D

If we take graphene as a traditional 3-D system, the conductivity can be written as

\[
\sigma = \frac{1}{R} \frac{L}{Wd} = \frac{I}{V_{bias}} \frac{L}{Wd} \quad \text{(Eq.1)}
\]

where L, W and d are the length, width and thickness of graphene, respectively.
The density of charge carriers in Graphene can be tuned by gate voltage which is coupled to graphene by the 300nm SiO$_2$ (Fig.5-3c).

\[ Q = CV_g = \frac{\varepsilon_0 \varepsilon_r WL}{t} V_g \] where \( t \) is the thickness of SiO$_2$.

We also have \( Q = enWLd \) where \( n \) is the 3-D density of charge carriers.

Therefore \( n = \frac{\varepsilon_0 \varepsilon_r V_g}{edt} \) (Eq.2)

Substitute Eq.(2) and Eq.(1) into

\[ \mu = \sigma / ne = \frac{I}{V_{bias}} \frac{L}{Wd} \frac{dt}{\varepsilon_0 \varepsilon_r SiO_2 V_g} = \frac{I}{V_{bias}} \frac{L}{W} \frac{t}{\varepsilon_0 \varepsilon_r SiO_2} \frac{1}{V_g} \] (Eq.3)

2) 2-D

If we take graphene as a 2-D system, the conductivity can be rewritten as

\[ \sigma = \frac{I}{V_{bias}} \frac{L}{W} \] (Eq. 4)

The density of charge carriers in Graphene can be tuned by gate voltage which is coupled to graphene by the 300nm SiO$_2$ (Fig.5-3c).

\[ Q = CV_g = \frac{\varepsilon_0 \varepsilon_r WL}{t} V_g \] where \( t \) is the thickness of SiO$_2$.

We also have \( Q = enWL \) where \( n \) is the 2-D density of charge carriers.

We therefore have \( n = \frac{\varepsilon_0 \varepsilon_r V_g}{et} \) (Eq.5)

Insert Eq.4 and Eq.5 into the follow equation

\[ \mu = \sigma / ne = \frac{I}{V_{bias}} \frac{L}{W} \frac{d}{\varepsilon_0 \varepsilon_r SiO_2 V_g} = \frac{I}{V_{bias}} \frac{L}{W} \frac{t}{\varepsilon_0 \varepsilon_r SiO_2} \frac{1}{V_g} \] (Eq.6)

Comparing Eq. 3 and Eq.6, we obtain the same form for mobility by taking graphene as either a 2-D or a 3-D system.
We take graphene as a 2-D system and plot the conductivity of a graphene device vs. gate voltage in Fig.5-10. Since the charge carriers have a linear dispersion relation, the conductivity of graphene should increase linearly with back gate voltage. However, we find an obvious nonlinear behavior in Fig.5-10 which is caused by several reasons. The first reason is that the graphene is not a strict pristine 2-D system due to ripples in the third dimension, interaction between the graphene and SiO$_2$ substrate, and impurities from fabrication and environment.\textsuperscript{127} Short scatterings originated from these factors\textsuperscript{127} are independent of gate voltage and thus contribute to the nonlinear behavior in Fig.5-10. A second reason for this nonlinear behavior is the contact resistance (also independent of gate voltage) is incorporated in this figure. Due to these reasons, the resistivity of graphene is a combination of short-range scatterings and long-range scatterings while long-range scatterings are contributed only by the screening effect of charge carriers (linearly correlated with $V_g$) that accounts for the linear behavior.\textsuperscript{127}

![Figure 5-10 Conductivity vs. $V_g$ of the same graphene device.](image)
Figure 5-11 The resistivity originated from long-range and short range scatterings. Since the short-range scattering for electrons and holes are different, we subtract two different values of short-range scatterings from the resistivity to guarantee long-range scatterings for electrons (the part for 810Ω) and hole (the part for 250Ω) linearly correlated with $V_g$. A green dash line (“Combined”) is plotted for guidance of the eye.

Based on the argument above, the resistivity of the graphene device can be written as

$$\rho = \rho_L + \text{const}$$

where “const” includes shorting range scattering and the contact resistance.

Properly choosing the value of “const” can guarantee $1/\rho_L$ is linearly correlated to $V_g$ for either electrons (black line in Figure 5-11) or holes (red line in Figure 5-11). The mobility for both electrons and holes is $5500\text{cm}^2/\text{Vs}$, a value extracted from the linear part of the green dashed line using Eq.4.

5.5 Intrinsic response of graphene vapor sensors

(The following is from a manuscript that is under review at Nano Letters)
Figure 5-12 (a) AFM image of a graphene device. (b) Device schematic. (c) AFM line scans of the same device after exfoliation (black data; 0.8 nm thickness), after electrode fabrication by e-beam lithography (EBL) (blue data, ~ 2 nm thickness) and after a cleaning bake at 400°C in Ar/H\textsubscript{2} (red data, 0.8 nm thickness). The Ar/H\textsubscript{2} cleaning process removes the residue of the EBL resist. (d) Measured electrical conductivity versus gate voltage for the device before and after cleaning (red and black data, respectively). The cleaning step leads to significantly improved electronic properties.

Graphene is a zero bandgap semimetal with extraordinary electronic\textsuperscript{123, 124, 127, 133, 134} and mechanical properties\textsuperscript{135}. Comprised of a single layer of carbon with every atom on its surface, graphene is a purely two-dimensional material and an ideal candidate for use as a chemical vapor sensor. It has been reported that the absorption of individual gas
molecules onto the surface of a graphene sensor leads to a detectable change in its electrical resistance\textsuperscript{129}. It is known, however, that typical nano-lithographic processes can leave an uncontrolled residue on graphene\textsuperscript{136} whose impact on device transport and vapor sensing properties has not been fully explored. Moreover, the \textit{intrinsic} sensitivity of graphene to gaseous vapors can only be determined through the use of samples where contamination from lithographic processing has been measured and verifiably removed. Graphene vapor sensors that are known to be free of chemical contamination should then be amenable to (bio)molecular surface modification to control their chemical sensitivity, as has been done for carbon nanotubes\textsuperscript{137} and semiconductor nanowires\textsuperscript{138}. They should also prove amenable to quantitative modeling of their sensor characteristics\textsuperscript{128}.

In this section, we report on experiments where the structural and electron transport properties of a graphene field effect transistor (FET) were measured immediately after mechanical exfoliation, after contact fabrication using electron beam lithography (EBL) and thin film deposition, and after a cleaning process based on that suggested in Ref. \textsuperscript{136}. We find that standard EBL processing left the graphene covered by a $\sim$1-nm thick contamination layer that has a substantial impact on the transport properties and vapor sensor responses of the device. The contamination layer was removed by a high temperature cleaning process in a reducing (H\textsubscript{2}/Ar) atmosphere, enabling measurements of the properties of the pristine device. Compared to the as-fabricated (contaminated) device, we find that the clean device has roughly one-third the concentration of doped carriers, four-times higher carrier mobility, and much weaker electrical response upon
exposure to chemical vapors. An electrical current annealing process has been found to provide similar improvements in chemical doping and carrier mobility.\textsuperscript{133, 139, 140}

Samples were made using mechanical exfoliation to deposit graphene sheets onto an oxidized silicon substrate (300 nm oxide thickness) with prefabricated gold alignment markers. Few-layer graphene sheets were identified by optical microscopy\textsuperscript{121} and located with respect to the alignment markers. Atomic Force Microscopy (AFM) was used to measure the graphene thickness. Au/Cr source and drain electrodes were then fabricated using EBL and thin film evaporation. Polymethylmethacrylate (PMMA) was used as the electron beam resist (Microchem Corp., C4 950); the resist was exposed with a 30keV electron beam at a dose of 500μC/cm\textsuperscript{2} and then developed according to manufacturer instructions. After electrode deposition by thermal evaporation and a liftoff step, the surface topography was again measured by AFM, showing evidence of contamination, presumably by residual electron beam resist (see below). We conducted current-gate voltage (I-V\textsubscript{G}) measurements of the device using the p\textsuperscript{++} Si substrate as the back gate, and measured changes in electrical current upon exposure to chemical vapors at varying concentration. At this point the sample was cleaned by heating in flowing H\textsubscript{2}/Ar (850 sccm Ar, 950 sccm H\textsubscript{2}) at 400 °C for 1 h.\textsuperscript{136} Finally, AFM, electron transport, and vapor response data were collected on the cleaned sample for comparison with that obtained from the contaminated device. For the vapor response measurements, gas flows containing analyte vapors of known concentration were created using a bubbler system, as described previously.\textsuperscript{18} High purity nitrogen was used to flush the device between
exposure to analyte-containing gas flows.

Figure 5-13. Measured sensor responses, before (black) and after (red) sample cleaning, to vapors of (a) water, (b) nonanal, (c) octanoic acid, and (d) trimethylamine. The cleaning step removes resist residue from the lithography step and enables the measurement of the intrinsic responses of the graphene device. Insets: Sensor responses to water vapor and TMA show a power law dependence. Power laws are 0.38 (TMA) and 0.79 (water)

Fig 5-12a shows the AFM image of a typical graphene sample, shown schematically in Fig.5-12b. The as-exfoliated graphene film is 0.8 nm thick, and therefore presumed to be a bilayer (Fig.5-12c, black line scan data). After EBL, the measured thickness is 1.8
nm (Fig. 5-12c, blue data), with the thickness increase attributed to the presence of PMMA residue. From the I-V$_G$ characteristic (Fig. 5-12d, red data), and assuming a combination of short-range and long-range carrier scattering we find a carrier mobility of 1600 cm$^2$/V-s (see Section 5.4). The I-V$_G$ characteristic is hysteretic, similar to that of carbon nanotube FETs, where it was attributed to charge injection into surface traps. The charge neutrality point (point of minimum conductivity) occurs at $V_G \approx 30 \, V$, corresponding to a doped carrier density of $2.2 \times 10^{12}$/cm$^2$ at $V_G = 0$.

We see profound changes in the AFM data and the electrical transport measurements after the cleaning bake. AFM line scans show a sample thickness of 0.8 nm, exactly equal to that of the as-exfoliated graphene (Fig. 5-12c, red line scan data). From the I-V$_G$ data (Fig. 5-12d, black data), we find that the carrier mobility has increased by a factor of approximately four to 5500 cm$^2$/V-s, and that the doped carrier density at $V_G = 0$ has been reduced by two-thirds to $7.0 \times 10^{11}$/cm$^2$. The hysteresis in the I-V$_G$ is much smaller than that observed before the cleaning step. We conclude that the resist residue leads to carrier doping into the graphene, increased carrier scattering, and a larger density of trap states for the carrier injection that leads to greater I-V$_G$ hysteresis. The cleaning step is effective at significantly improving the structural and electronic properties of the graphene.

We find that the cleaning procedure leads to equally dramatic changes in the electrical response of the device upon exposure to chemical vapors at various concentrations (Fig. 5-13). The analytes used were water vapor, nonanal, octanoic acid,
and trimethylamine (TMA). After the EBL processing and before the cleaning bake, the device shows strong electrical response to these chemical vapors, even at concentrations in the part-per-billion range in the case of octanoic acid. The responses and recovery are rapid (tens of seconds) and reversible without heating or other refreshing, although irreversible “poisoning” of the sensor response is seen upon exposure to water at a concentration of 40% of a saturated vapor (Fig.5-13a).

The signs of the measured vapor responses are in agreement with a model where the resist contamination acts as an unintentional “functionalization” layer that absorbs analyte molecules while the p-type graphene device provides a high-sensitivity electronic readout. Water vapor is an oxidant under typical conditions (indeed, it has been suggested that the p-type behavior of graphene samples under ambient may be due to the effect of adsorbed water\textsuperscript{143}), so exposure to additional water vapor is expected to increase the hole density and the current. Octanoic acid will deprotonate in the presence of adsorbed water, increasing the hole concentration (and thus the current) in the graphene by “chemical gating”.\textsuperscript{144} Trimethylamine is a proton acceptor in the presence of water, so a current decrease is expected, consistent with our observations. At this point it is unclear whether the nonanal response is consistent with this picture. The current response typically follows a power law dependence on concentration, with the exponent in the range of 0.4 – 0.8 (insets in Fig.5-13). Similar power law behavior has also been reported for vapor sensors based on metal oxides\textsuperscript{145,146} and conducting polymer nanowires.\textsuperscript{147}

The electrical responses to chemical vapors are reduced by one to two orders of
magnitude after the cleaning bake. This observation is strong evidence that the EBL resist residue acts as an absorbent layer that concentrates molecules from the vapor within the polymer, less than 1 nm from the surface of the graphene. This behavior is not surprising since polymer films are sometimes used intentionally as analyte concentrators, for example in gravimetric vapor sensors based on surface acoustic wave devices.¹⁴⁸

The results presented here illuminate a pathway towards the application of intentionally functionalized graphene devices as nanoscale sensors of molecular analytes in the vapor and liquid phase. The two-dimensional nature of graphene typically leads to devices with lower electrical noise, and thus lower detection limits, than those based on one-dimensional nanomaterials (e.g., carbon nanotubes and semiconductor nanowires). For example, the data in Fig.5-13 imply that detection of carboxylic acids and aldehydes at ppb levels should be readily attainable. The graphene surface must be clean, however, before strategies to control its chemical affinity via molecular functionalization may be exploited. Because of the similarity of the two nanomaterials, the cleaning process demonstrated here should enable the ready transfer to graphene of surface chemistry modifications previously applied to carbon nanotubes for targeted molecular sensing in the vapor and liquid phases.

Summary

This chapter first introduced the history and properties of graphene. It then illustrated the mechanical exfoliation of graphene from bulk graphite, followed by the device
fabrication by EBL and the approach to extract charge carrier mobility. In the end, this chapter focused on the electronic properties and intrinsic response of graphene as a chemical gas sensor. It was found that the 1nm thick PMMA left by EBL degraded the mobility of graphene but acted as an analyte concentrator that improved the sensitivity of graphene sensors by one to two orders of magnitude.
Chapter 6
Summary and future work

6.1 Summary

The work in this thesis can be divided into three parts. The first part has investigated properties of single nanowire sensors. In the second part, we integrated heterogeneous nanowire sensors. The work in these two parts has demonstrated the feasibility of developing a sophisticated E-nose using the method proposed in the second part. The third part of the work independent of the first two parts has investigated the electronic and gas-sensing properties of graphene sensors.

In the first part, we synthesized conducting polymer PEDOT/PSS and metal oxide TiO₂ nanowires using electrochemical-templating method. All these nanowires were several micrometers long and approximately 150nm in diameter. TiO₂ nanowire devices were made contact with by standard Ebeam lithography. To make PEDOT/PSS nanowire devices, we positioned these nanowires onto prefabricated electrode gaps by dielectrophoretic assembly instead of lithography involving chemicals and high-energy beams that are harmful to our polymer nanowires. These nanowires were also intentionally synthesized in a striped structure gold-PEDOT/PSS-gold to guarantee intrinsic contact between polymer and electrodes. We then investigated the electronic properties of these nanowire devices. We found the resistance of TiO₂ decreased from several GΩ at room temperature to several hundred MΩ at 250°C. The current was
nonlinearly correlated to the bias voltage due to Schottky barriers. The activation energy of the TiO₂ nanowire was extracted to be 0.5eV. For PEDOT/PSS nanowire devices, the current is linearly correlated to the voltage with a resistance typically 100kΩ. The contact resistance between the polymer and gold was extracted to 27.6kΩ and the conductivity of PEDOT/PSS was 11.5S/cm. When used as chemical gas sensors, TiO₂ nanowires must work at a temperature higher than 200°C while the conducting polymer has a degraded sensitivity at elevated temperatures. In terms of sensitivity, all these sensors were only comparable to thin film sensors of the same material because these nanowire sensors still had a relatively large size. However, their response to analytes was ten times faster than the later. This part of work laid an important foundation for the heterogeneous integration.

In the second part of the work, we proposed and demonstrated an electrochemical approach that could integrate nanowires of different materials together. This approach can meet all the requirements to develop the “front end” of a sophisticated electronic nose system. It started with the fabrication of an on-chip nanochannel template with each channel connecting to its electrode. As demonstrated in the first part, different types of nanowires could be synthesized electrochemically inside different channels by controllably addressing different electrodes. In experiments we integrated silver, tin and gold nanowire arrays on the chip. Additional features such as integrating two- and multi terminal nanowires were also achieved using this method. At the end of this part, we proposed to integrate nanowire sensor arrays with CMOS circuits and analyzed the
challenges of this integration. The major challenge was the operating temperature incompatibility of different sensors and CMOS circuitry. The well-developed microhotplate technology was proposed as a solution to this challenge. With this part of work, we have moved one more step closer to the development of a sophisticated Enose system.

The third part work is independent of the previous work. In this part, we explored the electronic and gas-sensing properties of graphene. Single-layer graphene sheets were first deposited onto silicon wafer using the mechanical exfoliation method and then made contact by conventional nanolithographic process. It is known, however, that the nanolithographic processing typically left a resist residue on the graphene surface, whose impact on the sensor characteristics of the system has not yet been determined. In this part of work, we showed that the contamination layer both degrades the electronic properties of the graphene and masks graphene's intrinsic sensor responses. The contamination layer chemically doped the graphene, enhanced carrier scattering, and acted as an absorbent layer that concentrates analyte molecules at the graphene surface, thereby enhancing the sensor response. We demonstrated a cleaning process that verifiably removes the contamination on the device structure and allows the intrinsic chemical responses of graphene to be measured. As a part of future work, it will be very interesting to explore the molecular functionalization of the cleaned graphene.

6.2 Future work
The immediate follow-up to the work in this thesis is to integrate TiO$_2$, ZnO and/or SnO$_2$ nanowire sensors on the same chip using the method demonstrated in Chapter 4. Tens of these nanowires can be electrically monitored using off-chip multiplexers. To test the capability of distinguishing analytes, we should expose these nanowire sensors to tens of analytes including O$_2$, H$_2$, CH$_4$, CO, CO$_2$, NO$_2$, NO, and organic analytes (acetone, ethanol, methanol, etc.) at elevated temperatures. Neural network technique should be applied to analyze the data.

To enhance the smartness of the nanowire array, we need to increase the chemical diversity of these nanowires. Due to the temperature incompatibility, it is obviously impossible to integrate metal oxide and conducting polymer nanowires on a chip without microhotplates. With a single category of materials, we can develop doping technique to increase chemical diversity. Since all our nanowires are synthesized by electrochemical-templating method, it is very necessary to dope the wires with widely used dopants during the electrochemical process, such as Pd doped SnO$_2$ and Cl-doped polyaniline. As far as we know, this doping technique is quite new and will generate a big impact on nanowire synthesis. A nanowire array consisting of either doped metal oxides or doped conducting polymers can be constructed and tested.

After having achieved the two aforementioned stages, we can upgrade the research on Enose development to next level: a heterogeneous nanowire array chip with embedded multiplexers and microhotplates. Nanowire sensors of various materials and their doped counterparts can be integrated on the microhotplates that can locally control the
temperature. Tens of thousand nanowires with a chemical diversity of 20 to 50 including metal oxides, conducting polymers and their doped counterparts can be integrated and individually addressed. Gas-sensing data should be recorded on such a chip that is unprecedented.

In Chapter 5, we found a single layer of PMMA residue can chemically dope the graphene sensor and therefore enhanced its gas-sensing response while a cleaned graphene sensor had significantly reduced sensitivity. The results illuminate a pathway towards the application of intentionally functionalized graphene devices as nanoscale sensors of molecular analytes in the vapor and liquid phase. The two-dimensional nature of graphene typically leads to devices with lower electrical noise, and thus lower detection limits, than those based on one-dimensional nanomaterials (e.g., carbon nanotubes and semiconductor nanowires). For example, the data in Fig.5-13 imply that graphene sensors show rapid response and recovery, and that detection of carboxylic acids and aldehydes at ppb levels should be readily attainable. The graphene surface must be clean, however, before strategies to control its chemical affinity via molecular functionalization may be exploited. Because of the similarity of the two nanomaterials, the cleaning process demonstrated here should enable the ready transfer to graphene of surface chemistry modifications previously applied to carbon nanotubes for targeted molecular sensing in the vapor and liquid phases.
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