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Nanostructures, such as nanowires, nanocolumns, and nanotubes, have attracted a lot of attention because of their huge potential impact on a variety of applications. For sensor applications, nanostructures provide high surface area to volume ratios. The high surface area to volume ratio allows more reaction areas between target species and detection materials and also improves the detection sensitivity and response time. The main goal of this research was to exploit the advantages and develop innovative methods to accomplish the synthesis of nanowires and nano-coulnm conducting polymers used in humidity detection. To accomplish this, two fabrication methods are used. The first one utilizes the geometric confinement effect of a temporary nanochannel template to orient, precisely position, and assemble Polyaniline (PANI) nanowires as they are synthesized. The other approach is to simply spin-coat a polymer onto a substrate, and then oxygen plasma etch to generate a nano-columned Polyethylenedioxythiophene (PEDOT) thin film. 200 nm silicon oxide coated wafers with embedded platinum electrodes are used as a substrate for both fabrication methods. The biggest advantage of this first method is that it is simple, requires a single-step, i.e., synthesizing and positioning procedures are carried out simultaneously. The second method is potentially manufacturable and economic yet environmentally safe. These two methods do not produce extra nano-building materials to discard or create a health hazard.

Both PANI nanowires and nano-columned PEDOT films have been tested for humidity detection using a system designed and built for this research to monitor response (current changes) to moisture. To explain the surface to volume ratio effect, 200
nm PANI nanowires and 10 μm PANI wires were directly compared for detecting moisture, and it was shown that the PANI nanowire had a better sensitivity. It was found difficult to monitor the behaviors of the PEDOT reaction to varying moisture levels because even low humidity levels saturate the sample surface within a few minutes. Because of this, it was not perfect to distinguish the effects of etching the PEDOT film for humidity detection and difficult to apply nano-columned PEDOT films as a humidity sensors under continuously changing humidity conditions. However, nano-columned PEDOT films showed excellent performance in simulated breath tests, i.e., an area where the medical needs sensors for pulmonary monitoring.

Since the polymers are sensitive to heat, it was important to characterize the influence of temperature on the sensor performance. PANI nanowires and nano-columned PEDOT sensors were tested in the environmental chamber developed in this work as a function of temperature with the humidity fixed, and only the temperature was varied. The PANI nanowires showed very fast degradation at temperatures above room temperature, while the nano-columned PEDOT film performed up to 50 °C. The influence of other gases was also tested for the potential of gas sensing, selectivity, and chemical stability. In order to exclude the moisture effect during the measurement, the samples were characterized under the lowest humidity condition, RH 14 % preserved in the system. Under these conditions the PANI nanowires responded to the gases (hydrogen and carbon monoxide were used), but the moisture inside the PANI nanowire was forced to influence the gas detection. Therefore, samples were dried overnight under a nitrogen environment and tested again. With this careful control of the moisture
present, it was found that PANI nanowires respond to both hydrogen and carbon monoxide gases, however, there is no selectivity between gases. Nano-columned PEDOT films were also tested under the same experimental moisture-controlling conditions. It was shown that there was little response to other gases. Any response that may have been presented was buried in the electrical noise. Finally, both samples were tested for long-term stability. PANI nanowires showed almost linear degradation with continuous use, while nano-columned PEDOT was stable over extended periods of time. The PANI nanowires were more reactive to the environment compared to the nano-columned PEDOT films. The only disadvantage of the nano-columned PEDOT sensor structure is that it loses its durability when it is directly exposed to liquid water or highly saturated humidity for long periods of time. A surface treatment of PEDOT was developed that enhanced its durability against water without degrading its sensor performance. Nano-columned PEDOT films look promising for breath sensors for medical usage because they have sub-second response times and are relatively chemically and physically stable.
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To My Family
Chapter 1

INTRODUCTION

1.1 BACKGROUND

Humidity sensors have gained increasing applications in industrial processing and environmental control [1]. For manufacturing highly sophisticated integrated circuits in the semiconductor industry, humidity or moisture levels are constantly monitored in wafer processing. There are also many domestic applications, such as intelligent control of the living environment in buildings, cooking control for microwave ovens, intelligent control of laundry, etc. In the automobile industry, humidity sensors are used in rear-window defoggers and motor assembly lines. In the medical field, humidity sensors are used in respiratory equipment, sterilizers, incubators, pharmaceutical processes, and biological products. In addition, the medical field would like to use them for patient pulmonary monitoring. In agriculture, humidity sensors are used for greenhouse air-conditioning, plantation protection (dew prevention), soil moisture monitoring, and cereal storage. In general industry, humidity sensors are used for humidity control on chemical gas purification, dryers, ovens, film desiccation, paper and textile production, and food processing.

Humidity measurements can be expressed in several different ways including absolute humidity (mass of water vapor per unit volume), the dew point (td, the temperature at which the water vapor pressure is equal to the saturation water vapor pressure, expressed in °C or °F), and more often, the relative humidity (RH) (the percent
The ratio of existing water vapor pressure \( (p) \) to the saturation water vapor pressure \( (p_s) \), \( \frac{p}{p_s} \times 100 \). The humidity level sometimes can also be expressed in PPMv (the ratio of the partial of pressure to the total pressure minus the partial pressure of the water vapor multiplied by \( 10^6 \)), specific humidity (the mass of water vapor per unit mass of natural air), and the mixing ratio (the mass of water vapor per unit mass of dry air). Figure 1-1 shows the correlation among Relative Humidity (RH), Parts Per Million by volume (PPMv), and the Dew/Frost Point (D/F PT) [2]. RH measurement covers the upper humidity range, PPMv covers the lower humidity range, and D/F PT covers the entire humidity range. For daily life, relative humidity is typically used for ease of understanding. For trace moisture measurements, it would be better to use PPMv or D/F PT, because it tells us the absolute amount of water vapor in a gas or air.

Figure 1-1: Correlation among humidity units: Relative Humidity (RH), Dew/Frost point (D/F PT), and Parts Per Million by volume fraction (PPMv) [2].
A wide variety of materials have been studied for use as sensing elements in humidity sensors and commercial devices. The choice of a suitable material should be based on its sensitivity to humidity, low hysteresis, and linearity over the entire range of humidity and temperatures. It is also important when selecting a material that its properties are stable over time, thermal cycling, and exposure to the various chemicals that are likely to be present in the environment.

The materials widely used in humidity sensors can be classified into four groups: electrolytes, piezoelectrics, organic polymers, and inorganic ceramics. At the present time, the materials for commercially developed humidity sensors are mainly resistive and capacitive type organic polymer film and porous ceramics due to their low cost and good performance.

Ceramics, in particular metal oxides, such as alumina, silica, zirconia, titannia, and ferrous oxides, and their composites are widely used as humidity sensing materials. They usually have porous structures or are in the form of a nano-tube prepared by sol-gel, powder sintering, anodization, or vacuum deposition. This type of sensor has high resistance to chemical attack, thermal stability, and fast response times, but their sensitivity and long term stability are problematic [3]. Ceramic humidity sensors can be classified as electronic-type humidity sensors based on semiconducting properties and ionic-type humidity sensors. The humidity sensing mechanism of electronic-type humidity sensors, which are able to operate at temperatures higher than 100 °C, is that water is chemisorbed and acts as an apparent electron donor at high temperatures, resulting in increased conductivity for n-type semiconductors and decreased conductivity for p-type semiconductors. The ionic conduction humidity sensors operate at lower
temperatures (< 100 °C) and their humidity sensing is related to water-adsorbing processes on their surfaces and subsequent ionization, which involves surface chemistry and surface morphology [4-5].

Humidity sensors based on polymers have several advantages over humidity sensors based on ceramics. For instance, they have better long-term stability, lower manufacturing costs, and they can be operated at room temperature. There are two types of polymer humidity sensors; capacitive and resistive types. Humidity sensing polymers for capacitive humidity sensors usually have high resistivity and low permittivity with dielectric constants in the range of 3-7. The adsorption of water on the polymer surface results in an increase of the measured capacitance due to the high relative permittivity of water (~80). The water adsorption sites are hydrophilic hydroxyl groups and carbonyl groups. Polymers, such as cellulose derivatives (acetate), polyimide, poly (methyl methacrylate) (PMMA), are typically used. These sensors can be operated in the range of 0 - 100 % RH at temperatures in the range of -40 °C to 180 °C [6]. Although capacitive polymer humidity sensors have demonstrated excellent sensing performance, they also have their limitations. For example, they have relatively expensive manufacturing cost, complicated electrical configurations, and high hysteresis compared to resistive polymer humidity sensors.

Resistive polymer humidity sensors are based on polyelectrolyte polymers with a hydrophilic ionic or charged polar group such as polystyrene sulfonate, poly (vinylpyridine), poly (tetrafluoroethylene), or polymers with mixtures of inorganic salts, such as polyethylene oxide doped with LiClO₃ and phosphonium salt-containing monomer, (vinylbenzyl) tributyl-phosphonium chloride (VTBPC). These polymers have
ions for charge compensation that are electrostatically bonded to the matrix. The absorption of water increases the mobility of these ions and consequently decreases the resistance [7-8]. The polyelectrolyte humidity sensor type exhibits a strong change in resistivity of up to four orders of magnitude over the humidity range of 0 ~ 90 % RH. However, polyelectrolyte materials are generally not durable; they are generally soluble in water, which limits their applications [9].

In order to solve the problems of polyelectrolyte materials, copolymers and mutually reactive copolymers have also been studied for humidity sensing [10]. However, the synthesis method is complicated, and their environmental stability is relatively low. Recently, humidity sensors based on conjugated polymers that are conductive polymers have attracted considerable attention because of their ease of synthesis and environmental stability. Some conjugated polymers of interest include: polypyrrole, polyaniline, polythiophene, and their derivative conducting polymers [11-13].

1.2 RESEARCH MOTIVATION

Recently, nanostructures such as nanowires, nanocolumns, and nanotubes, have attracted a lot of attention because of their huge potential impact on many applications. For sensor applications, the nanostructures provide a high surface area to volume ratio. The high surface area to volume ratio allows more reaction areas between target species and detection materials, and improves detection sensitivity and response time [14]. Most of the commercial humidity sensors based on polymers are thin film or porous polymers, which are less than a millimeter thick and their sensing principle is similar to that of
ceramic sensors. The film contains micro-pores for water vapor condensation and some of the measurable physical properties change due to the water absorption. The geometrical change of the active sensing material definitely enhances the performance of sensors [15]. Nanostructured polymers are promising for future alternative sensing materials in the sensors [16].

To realize the full potential of nanostructured materials as active sensing materials in the sensor, proper manufacturable methods are necessary. Over the past few years, one-dimensional nanostructures such as nanotubes, nanorods, nanofibers, and nanowires comprised of different materials have been synthesized and implemented into device applications. However, the significant obstacle in the application of these nanostructures has been the difficulty in handling, maneuvering, and integrating them to form a complete system [17-20]. The challenge still has to be faced due to the lack of post-synthesis processes suitable for the hierarchical organization of these nano-scaled building blocks into functional assemblies and, ultimately, useful systems. Additional processing and self-assembly techniques are needed to contact the nanostructures and form interconnected structures that increase complexity. Therefore, there is an urgent need for an engineering approach to improve the control of manufacturing, assembling, and orientation of these nanomaterials.

1.3 RESEARCH OBJECTIVES

The main goal of this research is to develop innovative methods to accomplish the synthesis of conducting polymer nanowires and nanocolumns used for humidity detection, characterization, and at the same time, the precise control of the nanostructured
polymers in an environmentally safe way. To accomplish this, two fabrication methods were explored. The first one utilizes the geometric confinement effect of a temporary empty nanochannel template to orient, precisely position, and assemble nanowires as they are synthesized. The other approach is simply spin coating a polymer onto the substrate, and subsequently plasma-etching the polymer to generate nano-columned structures. There are no two-step, synthesizing and then positioning, procedures in the approach of this thesis. Individual devices are characterized and tested for humidity detection using an experimental system designed and built as part of the research.

1.4 THESIS ORGANIZATION

The organization of this thesis is as follows:

Chapter 1 describes the background and motivation of the research and provides an outline of the research.

Chapter 2 gives an overview of the conducting polymers, especially, properties of polyaniline (PANI) and polyethylenedioxythiophene (PEDOT). Their synthesis methods, such as electrochemical polymerization and chemical polymerization are also explained. Various configurations of humidity sensors based on conducting polymers are reviewed, and customized humidity detection systems are introduced. Their interacting mechanism is also explained.

Chapter 3 describes the fabrication and characterization of the polyaniline (PANI) nanowires. A temporary nanochannel template was used to synthesize PANI nanowires, which is a duplicate of a master mold. The process flow of both the temporary template and the master mold is demonstrated. Two hundred nanometer silicon oxide wafers were
used as substrates, and the final substrate process flow and verification of electrodes are demonstrated. Since the temporary nanochannel template is hydrophobic, oxygen plasma activation of the open nanochannel template was carried out to make the inside of nanochannels hydrophilic. Then a precursor solution was introduced into the nanochannels for electrochemical polymerization. Finally, various characterizations of synthesized PANI nanowires are shown.

Chapter 4 describes the fabrication of nano-columned Polyethylenedioxythiophene (PEDOT) structures and their characterization. The process flow of spin coating and oxygen plasma etching of PEDOT is demonstrated. The characterization of nano-columned PEDOT is also presented.

Chapter 5 describes the application of the PANI nanowires and PEDOT nano-columns to humidity sensing. PANI nanowires and nano-columned PEDOT are tested for humidity detection. The surface to volume ratio effect and etching effect are explained in terms of humidity detection. In order to improve the durability of nano-columned PEDOT against water, surface treatments of PEDOT were carried out. Other environmental factors such as influence of temperature, other gases, and long-term stability are examined.

Chapter 6 gives a summary and discussion of the results obtained throughout the entire thesis research and suggests future research.
1.5 REFERENCES


15. Kurt D. Benkstein, Carlos J. Martinez, Guofeng Li, Douglas C. Meier, Christopher B. Montgomery and Steve Semancik, J of Nanoparticle Research, 2006 8: p. 809


OVERVIEW OF CONDUCTING POLYMERS

2.1 INTRODUCTION

Until about 30 years ago all carbon-based polymers were regarded as insulators. The idea that plastics could be made to conduct electricity would have been considered absurd. Indeed, plastics have been extensively used by the electronics industry because of their insulating property. They still are utilized as an inactive packaging and insulating material. This very narrow perspective is rapidly changing as a new class of polymers known as intrinsically conductive polymers or electroactive polymers are being discovered. Although this class is in its infancy, much like the plastic industry was in the 30’s and 50’s, the potential uses of these are quite significant.

In 1958, polyacetylene was first synthesized by Natta et al. [1] as a black powder. This was found to be a semiconductor with a conductivity between $7 \times 10^{-11}$ to $7 \times 10^{-3}$ S/m, depending upon how the polymer was processed and manipulated. This compound remained a scientific curiosity until 1967, when a postgraduate student of Hideki Shirakawa [2] at the Tokyo Institute of Technology was attempting to synthesize polyacetylene, and a silvery thin film was produced as a result of a mistake. It was found that 1000 times too much of the Ziegler-Natta catalyst had been used. When this film was investigated it was found to be semiconducting, with a similar level of conductivity to the best of the conducting black powders. Further investigations, initially aimed to produce
thin film graphite, showed that exposure of this form of polyacetylene to halogens increased its conductivity a billion fold. Undoped, the polymer was silvery, insoluble and intractable, with conductivity similar to that of semiconductors. When it was weakly oxidized by compounds such as iodine, it turned a golden color and its conductivity increased to about $10^4$ S/m.

Many chemists started to develop new types of conducting polymers due to their significant potential. Polypyrrole, polyaniline, polythiophene, and their derivative conducting polymers have recently been developed and become the focus of research. Generally, conducting polymers have conjugated bonding with alternating single and double carbon-carbon bonds along with backbone of the molecule. In conjugated bonding, the chemical bonding between two carbon atoms in the hybridization state $2sp^22p_z$ leads to one unpaired p orbital electron (the $\pi$-electron) per carbon atom, and the unpaired p orbitals of successive carbon atoms overlapping along the backbone leading to bonding and also electron delocalization. This $\pi$-electron delocalization is what provides the electric pathway of charge mobility along the backbone of the polymer. The essential structural characteristic of all conjugated polymers is the kind of quasi-infinite $\pi$-electron system extending over a large number of recurring monomer units. This feature results in materials with directional conductivity, strongest along the axis of chain [3]. Conjugated polymers are insulators in their neutral state due to a large band gap, but highly doped conjugated polymers can have their conductivity increased by more than 10 million times. The doping of conjugated polymers can result in a wide range of electrical conductivities shown in Figure 2-1. In addition, another way to enhance the electronic
conductivity is molecular ordering, because there are fewer conjugation-interrupting defects and easier inter-molecular communication [4]. Thus, conjugated polymers are promising materials for future applications in electronics and sensors due to their tunable electronic properties, low cost, environmentally stability, flexibility, lightweight, easy disposability and processibility [5]. Table 2-1 shows a summary of table for various conducting polymers’ characteristics.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>CONDUCTIVITY ( (\Omega^{-1} \text{ cm}^{-1}) )</th>
<th>STABILITY (doped state)</th>
<th>PROCESSING POSSIBILITIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene</td>
<td>( 10^3 - 10^5 )</td>
<td>poor</td>
<td>limited</td>
</tr>
<tr>
<td>Polyphenylene</td>
<td>1000</td>
<td>poor</td>
<td>limited</td>
</tr>
<tr>
<td>PPS</td>
<td>100</td>
<td>poor</td>
<td>excellent</td>
</tr>
<tr>
<td>PFV</td>
<td>1000</td>
<td>poor</td>
<td>limited</td>
</tr>
<tr>
<td>Polypyroles</td>
<td>100</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Polythiophenes</td>
<td>100</td>
<td>good</td>
<td>excellent</td>
</tr>
<tr>
<td>Polyacryilne</td>
<td>10</td>
<td>good</td>
<td>good</td>
</tr>
</tbody>
</table>

Table 2-1: The table of various conducting polymers’ characteristics, courtesy of Colin Pratt.
2.2 PROPERTIES OF POLYANILINE (PANI)

Although it was discovered over 150 years ago, only recently has polyaniline captured the attention of the scientific community due to the discovery of its high electrical conductivity. Among the family of conducting polymers, PANI is unique due to its ease of synthesis, environmental stability, and simple doping/dedoping chemistry. Although the synthetic methods to produce PANI are quite simple, its mechanism of polymerization and the exact nature of its oxidation chemistry are quite complex. PANI has been one of the most studied conducting polymers of the past 20 years.

PANI is a conducting polymer of the semi-flexible rod polymer family, which means it is an organic polymer converted to a conductive polymer by appropriate oxidations and doping. Polymerized from the aniline monomer, PANI can be found in one of three idealized oxidation states [6]: leucoemeraldine, emeraldine, and pernigraniline. The main polyaniline structure is shown Figure 2-2, where x equals the degree of polymerization (DP). Leucoemeraldine with n = 1, m = 0 is the fully reduced state. Pernigraniline is the fully oxidized state (n = 0, m = 1) with imine links instead of amine links. Emeraldine (n = m = 0.5) form of polyaniline, often referred to as emeraldine base (EB), is either neutral or only partially reduced or oxidized. Emeraldine base is regarded as the most useful form of PANI due to its high stability at room temperature and the fact that upon doping the emeraldine salt form of PANI is electrically conducting.
PANI has an electronic conduction mechanism that seems to be unique among conducting polymers, because it is doped by protonation as well as p-type doping, which results in the formation of nitrogen base salt rather than the carbonium ion of other p-type doped polymers [7].

The imine sites are protonated by acids HA to bipolaron (dication salts) form [8]. However, this undergoes a further rearrangement to form the delocalized polaron lattice, which is a polysemiquinone radical-cation salt. The structures at each stage of this process are shown in Figure 2-3 [9].
Although theoretical calculations have predicted that the bipolaron state is energetically more favored than polaron [8], it is widely agreed that polarons are the
charge carriers responsible for the high conductivity in polyaniline [10]. It has been proposed that the presence of coulombic interactions, dielectric screening and local disorder in the PANI lattice act to stabilize the delocalized polaron state [11]. It also has been shown that bipolaron states do exist in PANI, but they are few in number and are not associated with the conducting regions of the polymer [11].

The conductivity of PANI is dependent on the temperature [12] as well as humidity [13]. In general, attachment of functional group decreases the conductivity, whereas the formation of copolymers between aniline and functionalized aniline results in intermediate conductivity. In addition, the preparation conditions, particularly as they relate to the formation of structural defects and the polymer morphology, influence conductivity [14]. It has also been reported that the conductivity of PANI is dependent on the solvent where it is cast from or exposed to. This phenomenon has been referred to as secondary doping [15]. The solvent causes a change in the polymer conformation and results in increased conductivity.

However, the most significant dependence of conductivity of PANI is upon the proton doping level [16]. The maximum conductivity occurs when PANI is 50% doped by protons, to give the polaron lattice structure shown Figure 2-3. Under these conditions, the conduction mechanism is similar that of a semiconductor in that the electrons are thermally promoted to the lower energy unfilled bands, thereby enabling conduction [17].

The occurrence of a charge exchange phenomenon is necessary to produce the conductivity levels observed, even in 50% doped PANI, because of the presence of structural defects other than those caused by inadequate protonation of the nitrogen sites [18]. It is proposed that this involves inter-chain proton exchange as well as electron
transport. This explains the observed dependence of conductivity on the ambient humidity, as the presence of water within the polymer lattice would facilitate this proton-exchange phenomenon [18]. At doping levels higher than 50%, some amine sites are protonated, and at levels lower than this some imine sites remain unprotonated. In both instances, delocalization of the charge carriers over the polymer backbone is disrupted, thereby reducing the conductivity of PANI.

2.3 PROPERTIES of Polyethylenedioxythiophene (PEDOT)

Most of the interesting conducting polymers that have been developed over the past 25 years, those based on polyaniline, polypyrrole, polythiophenes, polyphenylenes, and poly (p-phenylene vinylene) have attracted the most attention. Of these, the polyaniline family stands out for its ability to form processable conductive forms at relatively low cost and in bulk quantities [19]. Unfortunately, great care must be taken when handling this material due to the possible presence of benzidine moieties in the polymer backbone, which might yield toxic (carcinogenic) products upon degradation [20]. Because of this, numerous industrial and academic groups have limited their research in polyaniline chemistry. While polypyrrole and polythiophene are possibly more environmentally friendly systems, they have the disadvantage of being insoluble and infusible. In order to overcome these problems, numerous substituted derivatives of these polymers have been developed that carry alkyl, alkoxy, and other substituents along their backbones [21]. By controlling main-chain architecture (e.g., regioregularity) [22] and pendant group chemistry (e.g., water-soluble sulfonates) [23], a broad variety of properties were made available from the parent systems.
During the second half of the 1980s, scientists at the Bayer AG research laboratories in Germany developed a new polythiophene derivative, poly(3,4-ethylenedioxythiophene), having the molecular structure shown in Figure 2-4 [24].

![Molecular structure of PEDOT](image)

**Figure 2-4**: Molecular structure of PEDOT [24].

Prepared using standard oxidative chemical or electrochemical polymerization methods, PEDOT was initially found to be an insoluble polymer, yet exhibited some very interesting properties. In addition to a very high conductivity (~300 S/cm), PEDOT was found to be almost transparent as an oxidize film and showed a very high stability in the oxidized state [25]. The solubility problem was subsequently circumvented by using a water-soluble polyelectrolyte, poly-styrene sulfonic acid (PSS), as the charge-balancing dopant during polymerization to yield PEDOT/PSS. This combination resulted in a water-soluble polyelectolyte system with good film-forming properties, high conductivity (~ 10 S/cm), high visible light transmission, and excellent stability [26]. Films of
PEDOT/PSS can be heated in air at 100 °C for over 1000 h with only a minimal change in conductivity [26]. This new system is currently known under its commercial name: BAYTRON P (changed to CLEVIOS P). Figure 2-5 shows the chemical structure of BAYTRON P [26].

![Chemical structure of Baytron P](image)

**Figure 2-5**: Chemical structure of Baytron P, which is a dispersion of the oxidized polymer PEDOT and the polyanion PSS in water [26].

One method of enhancing the properties of electroactive polymers, while simultaneously preparing useful materials, is through polymer blending. For example, polyaniline-camphor acid (PANI-CSA) blends with polymethylmethacrylate (PMMA) and nylon exhibit quite high conductivities (1~10 S/cm) at relatively low (ca. 1%) loading levels of the conducting polymer in the host [27]. This high conductivity is attributed to the formation of a continuous network of the conducting polymers, which is
phase separated from the host. These concepts have been extended to PEDOT/PSS blended with polar host polymers (polyvinylpyrrolidone, PVP) [28]. In this instance, treatments of the blend with a bivalent metal (e.g., Mg$^{2+}$) leads to ionic cross-linking and enhanced electrical properties at quite low (less than 10%) loading levels. In addition, the use of crystallization-induced phase separation between PEDOT/PSS with polyethylene oxide has been shown to form blends with continuous domains of PEDOT/PSS. These exhibit higher conductivities when compared to blends prepared with amorphous host polymers [29]. Another interesting characteristic of this blend is that the excess negative charge allows the material to be ionically (physically) cross-linked with multivalent cations such as Mg$^{2+}$ resulting in a conducting hydrogel, which is stable in aqueous media [29].

2.4 POLYMERIZATION TECHNIQUES

A range of polymerization techniques have now been developed, including electrochemical polymerization, chemical polymerization, photochemically initiated polymerization, enzyme-catalyzed polymerization, and polymerization employing electron acceptors. PANI and PEDOT are most commonly prepared through the chemical or electrochemical oxidative polymerization of the respective monomers in acidic solution or water. The following sections will explain the mechanism of electrochemical polymerization of PANI, and chemical polymerization of PEDOT.

2.4.1 Electrochemical polymerization of PANI
Electrochemical polymerization of PANI is routinely carried out in an acidic aqueous solution of aniline. This low pH is required to solubilize the monomer and to generate the emeraldine salt as the only conducting form of PANI. Potentiostatic or potentiodynamic techniques are generally employed to oxidize the monomer. The applied potential of 0.9 - 1.1 V (vs Ag/AgCl) during potentiostatic deposition has been reported to give more adherent films [30].

The appearance of defects due to over-oxidation of the polymer has been proposed, but the exact nature of the over-oxidation is not known. One theory is that cross-linking occurs [31], while another describes the opening of the chain after the formation of a paraquinone [32].

The generally accepted mechanism for the electropolimerization of aniline is shown Figure 2-6 [33]. Formation of the radical cation of aniline by oxidation on the electrode surface (step 1) is considered to be the rate-determining step. This is followed by coupling of radicals, and elimination of two protons. The dimer (oligomer) formed then undergoes oxidation on the electrode surface along with aniline. The radical cation of the oligomer couples with an aniline radical cation, resulting in propagation of the chain. The formed polymer is doped by the acid (HA) present in the solution (step 4).
The growth of PANI has been found to be self-catalyzing; the more polymer deposited, the higher the rate of polymer formation. A mechanism for this has been proposed, involving adsorption of the anilinium ion onto the most oxidized form of polyaniline, followed by electron transfer to form the radical cation and subsequent re-oxidation of the polymer to its most oxidized state [34].

Figure 2-6: The process of electrochemical polymerization of aniline [33].
2.4.2 Chemical polymerization of PEDOT

Chemical polymerization of PEDOT derivatives can be carried out using several methods and oxidants. The first method involves the chemical polymerization of alkylated or alkoxyated PEDOT derivatives resulting in regio-random PEDOT derivatives that are soluble in common organic solvents such as CHCl₃, CH₂Cl₂, and tetrahydrofuran (THF) [35-36].

A second polymerization method of PEDOT has been reported by de Leeuw et al [37]. Utilizing Fe(OTs)₃ at elevated temperature in combination with imidazole as a base, resulted in a black insoluble and infusible PEDOT film that, after rinsing with water and n-butanol, exhibited conductivities of up to 550 S/cm.

The third, and most practically useful polymerization method for PEDOT, is the so-called BAYTRON P (CLEVIOS P) synthesis that was developed at Bayer AG [26]. This method utilizes the polymerization of PEDOT in an aqueous polyelectrolyte (most commonly PSS) solution using Na₂S₂O₈ as the oxidizing agent. Carrying this reaction out at room temperature results in a dark blue, aqueous PEDOT/PSS dispersion, which is commercially available from Bayer AG under its trade name BAYTRON P (now changed to CLEVIOS P). An interesting aspect of BAYTRON P is that, after drying, the remaining PEDOT/PSS film is highly conducting, transparent, mechanically durable, and insoluble in any common solvent but soluble in water.

BAYTRON P was initially developed for antistatic application in the photographic industry. Nowadays, however, it serves as a multi-purpose conducting polymer blend for several applications. As a result it is available in different grades (e.g.,
BAYTRON P EL (VPAI 4083) corresponds to the electronic grade of BAYTRON P that has been developed specifically for light-emitting diode (LED) application).

2.5 OVERVIEW OF HUMIDITY SENSORS BASED ON CONDUCTING POLYMERS

Recently, the demand for humidity control has increased in fields such as air conditioning systems, electronic manufacturing and drying processes for ceramics and foods [38]. An ideal humidity sensor should have the following characteristics: high sensitivity, broad range of operation, durability, reproducibility, high speed and low cost [39]. The most widely used humidity-sensing materials include porous ceramics (e.g., TiO$_2$ and Al$_2$O$_3$) [40-41], polymers (e.g., polyimide and phthalocyanine) [42-43], and polyelectrolytes (e.g., sulfonated polysulfone and polyvinyl acetate) [44-45].

Conducting polymers films such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives, have been used as the active layers of sensors since early 1980s [46]. Their applications seem to be very promising for building up cheap and reliable sensors. In comparison with most of the commercially available sensors, which are based on metal oxides and operated at high temperature, the conducting polymer sensors have many improved characteristics. For instance, they have higher sensitivities and faster response times. Furthermore, they operate well at room temperature.

Most of sensors transform the concentration of analytes present into detectable physical signals such as currents, absorbance, mass, or other acoustic variables depending on the sensor’s configuration. After being exposed to the vapor of an analyte, the active sensing material of the sensor interacts with the analyte and causes physical or chemical
property changes of the sensing material. Detecting moisture can also be explained in terms of the above mechanism. The detailed sensing principles and configuration of sensors based on conducting polymers will be discussed in the following sections.

2.5.1 Configuration and sensing principles

2.5.1.1 Chemiresistors

A chemiresistor is the most common sensor type due to its simple configuration and cheap fabrication cost. The chemiresistor changes its electrical resistance when it is exposed to the chemical environment. This type of sensor is simple yet efficient. Generally, the sensor is composed of a pair of electrodes and an active layer, as shown Figure 2-7 [47].

![Diagram of a chemiresistor conducting polymer sensor](image)

Figure 2-7: The common configuration of chemiresistor conducting polymer sensor [47].

Since the change of electrical resistance is measured as an output, a simple ohmmeter can be used for collecting data. Generally, a constant current or voltage is
applied across the electrodes, and the change of the voltage or current signals are monitored respectively.

Chemiresistors are the most popular device configuration of sensors, and many commercialized devices are based on it. The related technologies, including fabrication and measurements, have been maturely developed. Thin films, fibers and bulk materials can be utilized as the sensing elements of chemiresistors and their output signals are resistances. Using a conducting polymer as the sensing film brings several advantages in device fabrication and operation. Conducting polymers are easy to be processed into films by many techniques as summarized above; most of these methods are operated at room temperature. The disadvantage of chemiresistor is that the resistance of a device is influenced by many ambient factors, and not only determined by the resistance of conducting polymer sensing film, but also the contact resistance of the electrodes. Moreover, little information other than resistance can be obtained; this is unfavorable in distinguishing different analytes.

2.5.1.2 Transistor sensors

The well known organic thin-film transistors (OTFTs) have been applied in the sensing field just after they were first developed [48]. In general, a TFT consists of a semiconductor active layer in contact with two electrodes (source and drain), and a third electrode (gate) that is separated with active layer by an insulating film. In operation, a source-drain voltage is applied and a source-drain current is measured. The gate is used to modulate the current by a gate potential. The source-drain current is changed when sensing film interacts with the analyte and shifts the threshold voltage of the device. Two
types of conducting polymer transistors, classified by whether the current flows through the polymer [49-50], have been used to detect analytes, as illustrated in Figure 2-8. Figure 2-8 (A) shows the structure of insulated gate field-effect transistor (IGFET), whose gate electrode is made of conducting polymer and the current flows through the other semiconducting layer, e.g. silicon, and Figure 2-8 (B) represents the configuration of thin film transistor (TFT), its active layer is made of conducting polymer.

![Figure 2-8: Configuration of IGFET (A) and TFT (B) [49-50].](image)

The modulation of source-drain current is interpreted as that an appropriate gate potential can enrich charge carriers in the semiconducting layer close to gate electrode, forming a current channel. When the two chemically different plates are electronically connected, an electric field is created at their interface. This field is proportional to the difference of work functions of the two plate materials [51], and both source-drain current and turn-on voltage are governed by it. Electron transfer between analyte molecules and sensing polymer is able to change the work function of the polymers, which causes response in source-drain current of gate voltage.
In comparison with chemiresistors, transistors provide more parameters for measurements, thus, may give more detailed information regarding the analyte chemical. Moreover, the detection limit and sensitivity of the sensors based on transistors are better than those of chemiresistors because of the signal amplification of transistor devices. The benefits of using conducting polymers as the sensing layer is the convenience in fabrication. Besides, easy modification in conducting polymer structures provides a facile route to sensing materials with different work functions and selectivity to analytes, which ensure high performance of transistor configured sensors. The disadvantages of these devices are, as other semiconductor devices, their preparation is slightly complicated and the characterization of a transistor is more difficult than a chemiresistor.

2.5.1.3 Optic devices

UV-vis and NIR spectra can reflect the electron configurations of conducting polymers. During the doping process, the spectral absorbance of conducting polymer film will change and new bands will appear due to the formation of polaron and bipolaron; while the spectrum can return to its original shape after dedoping [52]. Thus, exposing a conducting polymer to an analyte can be detected by recording the UV-vis or spectral changes. An ultra thin film is suitable for fabricating an optic sensor, because the spectrum of a thin film is easy to be recorded by using commercial spectrometers.

By using an optical fiber to measure the absorbance of the polymer layer, one can carry out long distance detection. Two typical configurations of optical devices are shown in Figure 2-9. One is placing the sensing film on the cross-section of the fiber as illustrated Figure 2-9 (A) [53]. The mechanism of this device is the same as that of direct
measuring techniques. The other is removing a small fraction of the cladding on the fiber and coating this section with conducting polymer, as shown in Figure 2-9 (B) [53].

Figure 2-9: Configuration of two typical optical sensors using optical fibers, (A) Placing the sensing film on the cross-section of the fiber, (B) Removing a small fraction of the cladding on the fiber and coating this section with conducting polymer [53].

Measuring the spectra of conducting polymers can help us to directly study their electron configuration. The sensor is only a piece of glass covered by a thin film of conducting polymer, whose configuration and fabrication procedures are very simple. However, the sensitivity of this kind of sensor is low, and the need of special spectrometers is expensive and inconvenient.
2.5.1.4 Piezoelectric crystal sensors

Two type of sensors fall into this category; they are quartz crystal microbalance (QCMB) and surface acoustic wave (SAW) sensors. A typical schematic diagram of QCMB is shown in Figure 2-10 [54]. It consists of a conducting polymer coated quartz crystal and a pair of electrodes. The resonant frequency of a quartz crystal changes with its mass load [54].

Figure 2-10: Configuration of quartz crystal microbalance sensor device [54].

A standard design for a SAW device is shown in Figure 2-11 [55]. A transmitter interdigital electrode (IDTs) and a receptor interdigital electrode are attached onto a piezoelectric crystal. The polymer film is coated on the gap between these two electrodes. An input ratio frequency voltage is applied across the transmitter IDTs, inducing deformation in the piezoelectric substrate. These deformations give rise to an acoustic wave, which transverse the gap between two IDTs. When it reaches the receptor IDTs, the mechanical energy is converted to a ratio frequency voltage [55]. The adsorption and desorption of analyte on the polymer film on the gap will modulate the wave propagation characteristics.
The detect limits of above two type of devices are very low (<1 ppm). Because the piezoelectric crystal is rather sensitive to mass uptake, adsorbing a very small amount of analyte can be detected through frequency change. For the same reason, the selectivity of piezoelectric crystal device is poor.

2.6 SUMMARY

The origin and history of conducting polymers have been briefly explained in this chapter. Among these conducting polymers, polyaniline (PANI) and Polyethylenedioxythiophene (PEDOT) are highlighted due to their ease of synthesis, environmental stability, and simple doping/dedoping chemistry. However, PANI is approached cautiously since the presence of benzidine moieties in the polyaniline backbone may yield toxic (carcinogenic) products upon degradation. Because of this, numerous industrial and academic groups have limited their research in polyaniline chemistry, while PEDOT is more environmental friendly with good film-forming properties, high conductivity, high visible light transmission, and excellent stability.
We have reviewed different configurations of sensors based on conducting polymers, and it seems that the chemiresistive type of sensor is simple yet has a relatively good sensing performance and low fabrication cost. PANI and PEDOT:PSS will be synthesized with our novel fabrication methods and built for chemiresistive type of humidity sensors, and then characterized and tested for moisture sensing performance in the following chapters.
2.7 REFERENCES


Chapter 3

FABRICATION OF POLYANILINE (PANI) NANOWIRES AND THEIR CHARACTERIZATIONS

3.1 INTRODUCTION

In order to enhance the performance of sensors, an attractive approach is to use a configuration that gives a high surface to volume ratio of the active materials. This is because it improves detection sensitivity and response time due to more reaction area for target species adsorption or absorption, and hence reduces diffusion time [1-2]. Nanowires are very promising structures for sensing due to their inherently very large surface to volume ratios. The small scale of these structures also allows for the high integration of many nanowires of different materials into array configurations thereby giving the potential of building sophisticated sensors with enhanced detection selectivity. Current approaches for fabricating nanowire sensors generally use two steps: a growth/synthesize step and a positioning/assembly step. However, most of the approaches for the second step are impractical and often time consuming [3-5]. In addition, the techniques are potentially environmentally hazardous since only a few out of a large number of grown nanostructures are used for the assembly and the unused nanostructures are discarded. Our group recently suggested a new fabrication approach, the Step-and-Grow technique, which builds devices by repeating the following procedures: positioning a template mold on electrodes, growing/synthesizing nanowires, and moving the template mold to next place [6]. The technique merges the two
commonly used fabrication steps into one, and does not produce any extra nanostructures that must be discarded. The specific fabrication processes and characterizations of polyaniline (PANI) nanowires made in this manor are now described.

3.2 PROCESS FLOW OF MOLD FABRICATION

3.2.1 Fabrication of the master mold

In order to fabricate a temporary nanochannel template, a master mold is necessary. The master mold designed for this study has 100 nanowires that will be used to form nanochannels in the temporary template. The substrate for forming the master mold is silicon, since conventional semiconductor processing techniques can conveniently process it. These silicon wafers began with a 1μm thick thermal oxide coating for obtaining the positive shape of pattern transfer. The dimensions of wire widths fabricated on this master mold were designed to be 100 nm, therefore direct write electron beam (e-beam) lithography is necessary. The e-beam resist (2% PMMA (Poly Methyl Methacrylate) 950K) was spin coated (4000 rpm/1000 RAMP for 60 sec) on the wafer and a 15 nm gold layer was deposited on top of the resist by thermal evaporation. This thin gold layer dissipates charges on the surface of sample and helps obtain precise feature sizes. After e-beam writing, the thin gold layer was etched by gold etchant solution less than 1 min and a 1:7=MIBK (Methyl isobutyl ketone):IPA (Isopropanol) solution was used for developing the exposed resist. A 25 nm chromium layer was deposited and then the resist was removed by lift-off under stripper (remover PG). This chromium layer is used as a dry etch mask in the subsequent etch process. The next step was dry etching of silicon oxide to get highly anisotropic features. The completed master
mold had an aspect ratio of 1:2 (width:height), or 100 nm : 200 nm. Finally, the chromium mask was removed by wet etching and the silicon oxide master-mold was obtained. The overall process flow is illustrated in Figure 3-1: (a) Sample preparation, (b) Direct e-beam writing, (c) Etching gold layer and developing e-beam resist, (d) Chromium layer deposition, (e) Lift-off of e-beam resist, (f) Dry etching of silicon oxide, and (g) Wet etching of chromium layer.

Figure 3-1: Illustration of the master mold fabrication procedures.
The dry etching tool (MERIE) used in this study was almost to be phased out and was not in the best of conditions, therefore, it was difficult to maintain the width of etched feature. Figure 3-2 shows a FESEM image of the master mold after fabrication.

![FESEM image of the master mold](image)

Figure 3-2: FESEM image of the master mold.

3.2.2 Fabrication of temporary nanochannel template

PDMS (Polydimethylsiloxane) was used as a template mold, which is currently the most widely used silicon-based organic polymer. Some of its applications include: contact lenses, medical devices, elastomers, caulking, lubricating oils and heat resistant tiles [7].

There are four reasons why PDMS is a good candidate for the temporary nanochannel template. The first is that PDMS is known for its unusual rheological (or
flow) properties for replication. This enables one too even replicate nano-scaled feature. The second is its optical transparency, which is useful when aligning a PDMS mold on top of electrodes. The mold is to be positioned on the middle set of electrodes in Figure 3-3 to synthesize nanowires. Therefore, being able to optically see through the mold reduces error in mold positioning. The third reason is its good chemical durability. The molds can be treated with various chemical solutions without degradation or losing shape, thereby enabling the synthesis of different types of nanowires. For instance, metal nanowires can be synthesized in the mold by using electroplating solutions. The last reason is its low cost and ease of synthesis.

![A transparent PDMS temporary mold](image)

Figure 3-3: An illustration of the aligned PDMS temporary template on the electrodes.

It has been reported that the “ceiling” of an empty (open) PDMS nanochannel template can be easily collapsed [8]. If collapsing occurs, it is impossible to have chemical solutions permeate fully into the empty nanochannels. Actually, due to the aspect ratio used here (1:2), our nanochannel structures could potentially collapse at
either the ceiling or the sidewalls. To avoid such a collapse, a double layer PDMS structure was employed. The first layer, typically called hard-PDMS or h-PDMS, is a very brittle and rigid material and is capable of sustaining the inside of the channel structure [9]. The second layer, called s-PDMS (common PDMS), is relatively soft compared to h-PDMS. These materials are compatible with one another and together form a structure that retains most of the qualities of s-PDMS without the problem of channel collapse.

Four chemicals are needed to prepare the h-PDMS: two copolymers, VDT (7.0-8.0% Vinylmethylsiloxane, Dimethylsiloxne Copolymer, Trimethylsiloxy Terminated), HMS (25-30% Methylhydrosiloxane Dimethsioxane Copolymer, Trimethylsioxane Terminated), and two modulators, or Platinum-Divinyl Tetramethyl-Disiloxane, Tetramethytletravinylicyclo-Tetrasiloxane. These chemicals were purchased from Gelest Inc. USA.

Before preparing h-PDMS, the master mold required a surface treatment with Tridecafluoro-Tetrahydrooctyl-Trichlorosilane (Gelest Inc. USA). This surface treatment was used to make the silicon oxide surface hydrophobic [10]. This treatment helps with the separation between the master mold and a h-PDMS template. In order to coat the anti-adhesion solution (Tridecafluoro-Tetrahydrooctyl-Trichlorosilane), a vacuum desiccator and small container are required. Since Tridecafluoro-Tetrahydrooctyl-Trichlorosilane is very toxic, this coating process must be done under a fume hood. The coating process is as following: drop 10 μl of the anti-adhesion solution into a small container and place it beside the master mold. Then pump down the desiccator to the mTorr pressure range and
wait for 3 hours until all the solution has evaporated from the container and onto the surface of the wafer.

After the surface treatment of the master mold, 3.4 g of VDT and 1 g of HMS were measured and prepared. Two modulators, 18 μl of Platinum-Divinyl Tetramethyl-Disiloxane and 5 μl of Tetramethyldivinylcyclo-Tetrasiloxane were then mixed with VDT inside a glove box under inert conditions. After mixing the VDT and HMS, the copolymers were immediately poured into the master mold and spin-coated at 1000 rpm /500 RAMP for 45 sec. The film was then cured at 65 °C for 5 minutes inside an oven. Next, s-PDMS was poured into a Petri dish where the master mold was located at the center. There were many air bubbles created during mixing the base and cure, but these bubbles were easily removed by placing the Petri dish inside a vacuum desiccatior for 30 minutes. The s-PDMS was then cured at 65°C for 3 hours inside an oven. During the curing process the h-PDMS and s-PDMS bond together and form a dual-layer template structure. The final step is the separation of the template from the master mold and cutting it to a proper size. The overall procedures are shown in Figure 3-4: (a) Anti-adhesion coating and spin coating of h-PDMS, (b) Curing h-PDMS at 60°C for 5 min, (c) Pouring s-PDMS and curing it at 60°C for 3hrs, and (d) Separating the PDMS template from the master mold.
3.3 FINAL SUBSTRATE PROCESS FLOW AND VERIFICATION OF ELECTRODES

The final substrate carrying the nanowires can be glass, coated metal foil, or plastic. In this work, silicon wafers were used as the substrate. There are three reasons why they are good candidates for a substrate. An oxide film of silicon wafer provides the hydrophilic surface that is helpful to introduce solution inside the activated nanochannel template. The second reason is the well-controlled flat surface. Flat surfaces enhance the adhesion between the template and substrate, hence, improving to secure solution inside the nanochannel template. The third reason is convenience of the fabrication process, because conventional semiconductor processing can be used to fabricate electrode patterns on silicon wafers. The last reason is their electrical insulating property.

The general fabrication process flow of the electrodes is as following: silicon wafers with a 100 nm thick silicon oxide layer were cleaned in acetone and isopropanol.
baths to remove any organics and were then rinsed with DI water. A nitrogen gun was used to dry the wafers, and those wafers were then baked at 105 °C for 5 min on a hot-plate to drive off any water vapor residing on the oxide surface.

The next step was spin coating with double layer photo-resist, LOR 5A (1st layer) and SPR 1813 (2nd layer) at 4000 rpm / 1000 RAMP for 60 sec. The wafers were baked again at 180 °C for 6 min and 105 °C after each spin coating, which is called soft bake. It is done to drive away the solvent from the spun-on resist, improve the adhesion of the resist to the wafer, and anneal the shear stresses introduced during the spin coating.

In order to obtain the pattern of electrodes, wafer should be exposed to UV light through the open window of the pattern in the photo-mask. An MA6 contact aligner was used for UV exposure for 4.5 sec, and the wafer was baked at 105 °C for 1 min 30 sec, to reduce sidewall roughness. The double layer photo-resist structure caused an undercut after 3 min soaking into developing solution (CD-26), because the first thin layer (LOR 5A) is dissolved more quickly than SPR 1813 at fixed time. This undercut structure is effective for metal lift-off processes, because it prevents the metal from forming a continuous film up the sidewalls of the resist; hence it reduces fencing.

There were two different patterns of photo-mask used here; one is a four-electrode pattern, and the other one is a six-electrode pattern shown in Figure 3-5. Electrical four-point measurements are necessary for characterizing the electrical conductivity of a PANI nanowire. The six-electrode pattern has an advantage in this type of electrical characterization, because most of PANI nanowires on the six electrodes only reached to the 5th electrode after electro-polymerization. In the case of a four-electrode pattern, most of PANI nanowires crossed the 3rd electrode, but only a few nanowires reached to the 4th
electrode, because there is no potential difference between the 1st electrode and 4th electrode once one of the PANI nanowires has reached to the 4th electrode.

In the sensor structures, the electrodes were required to be level with the oxide surface, otherwise, the monomer solution would leak out of the channels and polymerize. This would result in polymer wires with undesirable geometries and dimensions. Therefore, a two-step approach was taken to ensure a flat, smooth surface with little electrode protrusion above the substrate surface. First, a trench was etched into the exposed regions of the silicon dioxide using Magnetic Enhanced Reactive Ion Etching (MERIE) for 1 minute at an etch rate of 30 nm per minute. The depth of the trench was carefully monitored by ellipsometer measurements to verify the etched thickness. Next, a Titanium / Platinum (Ti/Pt) layer was evaporated to a thickness that just filled the etched trenches. Generally, 28 nm was deposited with 3 nm Ti and 25nm Pt due to 10 % less

Figure 3-5: Layout design of photo-masks, (a) 4 electrodes, and (b) 6 electrodes.
deposition of an evaporation tool in the NanoFab. After the metal evaporation, an atomic force microscope (AFM) was used to measure the step between electrodes and oxide. The tolerable measured step height was up to 7 nm. If the step height is over 7nm, the protruding metal prevented the mold to adhere completely with the surface and allowed monomer to escape under the mold causing loss of nanowire definition and positioning, bad electrical contact, and easy breakdown of the nanowire shown in Figure 3-6.

Figure 3-6: Illustrations of side effects due to the step of electrodes, (a) leakage of solution, and (b) Bad contact or easy to breakdown.

3.4 OXYGEN PLASMA ACTIVATION OF OPEN NANOCHANNEL TEMPLATE

Once the template mold and substrate electrode structures were prepared, an additional template treatment step was needed before the nanowire structures could be fabricated. This additional step was needed because, at this point, the hydrophobic surface of the PDMS template mold defining the three walls of the empty channel
structure did not allow the introduction of the PANI precursor solution into the channel structure. The surface of the PDMS channel walls must be made hydrophilic to draw-in the solution. Using an oxygen plasma activation exposure does this. This activation makes the open walls and ceiling of the nanochannel hydrophilic by changing the carbon and oxygen surface composition ratio without any physical damage or chemical deposition [11]. As the surface of the PDMS is exposed to oxygen plasma, the hydrophobic –OSi(CH₃)₂O- groups are changed to be hydrophilic –OₙSi(OH)₄₋ₙ- groups at the PDMS surface. The change of the chemical groups at the surface indicates the oxidation of the PDMS surface by replacing the methyl (Si-CH₃) group by the silanol (Si-OH) group [12-13]. In order to avoid wetting the region of PDMS template surface between empty channels, the oxygen plasma activation is done with the channel side of the template mold down as seen in Figure 3-7, i.e., the empty channels are in direct contact with the substrate. In this way, only the inner walls of the channel structures are exposed to the oxygen plasma. This selective exposure of the oxygen plasma makes only the inner walls of the channel structure become hydrophilic while the rest of the PDMS surface remains hydrophobic. Creating these two different types of surfaces on the template prevents the precursor solution from leaking under the template and between the channels, after the solution is introduced to the empty channel structures.
3.5 ELECTROCHEMICAL POLYMERIZATION OF POLYANILINE IN THE PDMS NANOCHANNEL TEMPLATE

The deposition and growth of polyaniline is based on well-known electrochemical oxidative polymerization, starting with monomer and electrolyte [14]. Aniline monomer was purified by distillation under reduced pressure prior to use and all solutions were made up just before use with Milli-Q grade water. In a typical experiment, the aligned nanochannel template on the electrodes was mounted on the probe station and the contact was established using a platinum probe between the 1\textsuperscript{st} electrode as the anode and 4\textsuperscript{th} electrode as the cathode (ground). The probe was pre-cleaned with isopropanol. A two-electrode setup was used for the deposition. A drop of 4 micro-liters of aqueous solution containing distilled 0.3 M aniline monomer in 1 M HCl was placed into the entrance of nanochannel template by a micropipette after mixing the solution in ultrasonic agitation. Once the solution front touched the channel opening, the solution was sucked into the nanochannels by capillary force. Special precautions were taken to avoid the spread of

Figure 3-7: Illustration of oxygen plasma activation, (a) channel down and activation, and (b) only inside of channel walls are activated.
solution around the template, which entrapped air bubbles in the middle of nanochannels and hinder the introduction of solution.

Electrochemical polymerization was accomplished potentiostatically at +1 V by using an HP 4156 semiconductor parameter analyzer, at room temperature. The 1st electrode used as the anode and the electropolymerization current was monitored simultaneously. The probe placed in the 4th electrode could be placed on the different electrodes for more spatially controlled polymerization. Figure 3-8 shows the current changes that occur throughout the electropolymerization process. The current increased until the PANI nanowires grew and reached to the last electrode (cathode). The heights and widths of the grown polyaniline nanowires replicate the dimensions of the nanochannels.

Figure 3-8: Plot of current vs. time during the electropolymerization of polyaniline nanowires. Wires were grown potentiostatically at 1V.
3.6 CHARACTERIZATION OF POLYANILINE NANOWIRES

As the electropolymerization potential was applied to the 1st electrode with the nanochannels filled with precursor solution, the PANI nanowires grew and deposited from the anode electrode (1st electrode) and elongated in the nanochannel with time. The range of applied potential was from 0.45 V to 1.2 V. The PANI nanowires were not synthesized under 0.45 V, while the electrical conductivity was low when potential was applied over 1.2 V. This phenomenon appears to be related to current density, which determines the degree of polymerization or oxidation state of monomer. Therefore, the applied potential needs to be changed depending on the dimensions and geometries being used. After growth of the PANI nanowires in the PDMS nanochannel template, the template was carefully removed while immersed in an isopropanol bath. This process should be carefully done for in order to re-use the PDMS template. After separation, the fully exposed PANI nanowires were characterized by visual inspection, chemical analysis, and electrical conductivity measurements.

3.6.1 Optical microscopy

Figure 3-9 shows an optical microscope image of PANI nanowires, where 47 of the possible 50 PANI nanowires were successfully grown in the PDMS. The precursor solution (distilled 0.2 M aniline monomer & 1 M HCl) was used for electropolymerization at 1.2 V. Here, the precursor solution was accidentally spread out around the template, hence, the PANI nanowires grew with two directions from the anode. The longest PANI nanowire is approximately 150 μm.
3.6.2 Field emission scanning electron microscopy

An FESEM (LEO 1530, NanoFab) was used to image the wires and Figure 3-10 shows an image of a PANI nanowire at 40000X. The width of PANI nanowire shown here is around 150 nm.

Figure 3-9: An optical microscopy image of PANI nanowires.
3.6.3 Atomic force microscopy

Figure 3-11 shows a 3D AFM image of PANI nanowire between two electrodes. The width of PANI nanowire is seems to getting thinner from bottom to top due to the shape of the temporary PDMS template, which is the duplicate of the master mold. The master molds did not have perfect anisotropic ratio due to the MERIE problems noted earlier. A further contribution to this wondering seenin Figure 3-11 is the size of AFM cantilever, which is less than 10 μm. By scanning the PANI nanowire with the cantilever, I could not get a precise profile of PANI nanowire. The original design of master mold was 100 nm by 200 nm, however, the AFM profile shown in Figure 3-12 is around 300 (bottom) nm by 300 nm.
Figure 3-11: A 3D AFM image of a PANI nanowire.

Figure 3-12: The AFM profile of PANI nanowire (Please note that X axis’ scale is micron meter).
3.6.4 Auger electron spectroscopy

The PANI nanowires on this study were too small to use Auger electron spectroscopy (AES) due to its limited spot size for characterization. Therefore, 10 micron wide PANI wires were used to verify the chemical composition of PANI. The synthesis condition was same with that of PANI nanowires; i.e., 0.3 M aniline with 1 M HCl was used as a precursor solution and electropolymerized at constant 1 V. Figure 3-13 shows the resulting AES spectrum showing the major composition of our PANI.

Figure 3-13: Auger spectrum of 10 micron PANI wires.
3.6.5 Conductivity measurements for single PANI nanowire

After polymerization and separation of the PDMS template, conductivity measurements for PANI nanowires were undertaken on a probe station using an HP 4156 semiconductor parameter analyzer at room temperature. For this characterization, single PANI nanowires exposed on the electrodes were electrically measured by using the electrodes in two-point and four-point configuration at room temperature. The calculated conductivity of PANI nanowire might not be precise due to its varying dimensions, however, we can estimate the contact resistance and resistivity of PANI nanowire.

3.6.5.1 Two-point measurements

The two-point measurements were carried out by using two platinum electrodes to measure current while sweeping voltage on the same electrodes. The contact resistance is included in the measured resistance in the two-point measurement configuration. Figure 3-14 shows the result of current-voltage (I-V) characteristics of the two-point measurement of single PANI nanowire. The dimensions of the PANI nanowire are 200 nm high, 150 nm wide, and 10 μm long between electrode 2 and 3, 40 μm long between electrode 1 and 4. The I-V curve is seen to be linear and goes through the origin, and the results are repeatable which indicates the conducting PANI nanowire did not degrade during the measurement. The slopes of the I-V curves are identical at positive and negative bias, which indicates no directional conductivity along the PANI nanowire. The conductivity obtained by the two-point measurement is 10 S/cm.
3.6.5.2 Four-point measurements

Four-point measurements were done using four adjacent platinum electrodes contacting the given PANI nanowire. These electrodes were all equally spaced 5 μm apart. In this case, the current was applied to the outer two electrodes (electrodes 1 and 4) and the resulting voltage differences between the inner two electrodes (electrodes 2 and 3) were measured. The four-point measurement eliminates all concerns about the voltage drop at the contacts and allows determination of the true conductivity of single PANI nanowire. Figure 3-15 shows the resulting I-V data obtained with the four-point
measurement. It is seen to be linear, to pass through the origin, and to yield a conductivity value of 17 S/cm. By comparing the four-point data with the two-point data, it may be seen that there is a high contact resistance between the platinum electrodes and the PANI nanowire. The calculated contact resistance was $1.17 \times 10^4$ Ohm.

Figure 3-15: I-V characteristics of single PANI nanowire whose dimensions are 150 nm wide, 200 nm high measured by an HP 4156 in the four-point measurement configuration.

3.7 SUMMARY

The use of a temporary (PDMS) nanochannel template for electrochemically synthesizing arrays of individual PANI nanowires with fully controlled dimensions, positioning, alignment, and electrical contacting has been demonstrated. During polymer growth in the template, the electrodes on the substrate covered with the template were
used to drive the electropolymerization in the empty nanochannels of template. After
growth, the template was carefully removed from the substrate, and then the fully
exposed PANI nanowire arrays were characterized. FESEM and AFM images verified
the dimensions of PANI nanowires in terms of the PDMS template. In addition, chemical
analysis showed the major composition of electrochemically grown PANI wires. The
resulting two-point and four-point electrical measurements, gave insight to the contact
resistance and conductivity of the PANI nanowires grown here.
3.8 REFERENCES

Chapter 4

FABRICATION OF NANO-COLUMNED PEDOT (Polyethylenedioxythiophene) STRUCTURES AND THEIR CHARACTERIZATION

4.1 INTRODUCTION

The high surface area to volume ratio holds the potential for improving the sensing performance of sensors, because it provides more reaction area compared to thin films. One-dimensional nanostructures such as nanowires, nanotubes, and nanoribbons are good examples of structures with high surface to volume ratios. Nanostructured thin films are another alternative structure with a high surface area to volume ratio. These films can be produced by vacuum techniques [1], from solution [2], by lithography and etching [3], and by coating onto nanostructures formed by imprinting or simply by assembled layers of nanoparticles [4]. Generally, the cost of nanostructured thin films manufactured by a vacuum technique is higher and conditioning the process parameters is also more complicated compared to the non-vacuum techniques like electrolytic and chemically deposited layers, polymer coatings, and coatings of dense layers of nanoparticles. Recently, non-vacuum techniques have gained more attention compared to vacuum techniques due to their simple processing and low cost. The applications of nanostructured thin films are not only used in sensors [5], but also in areas of optics [6], mechanics [7], and catalysts [8]. Now, the nanostructured thin films are recognized as a source of many new and practical application opportunities.
Our research group has developed a simple yet cost effective processing for fabricating nano-columned PEDOT thin films, which can be utilized as active sensing materials for sensors. PEDOT (CLEVIOS® P) is a ready-to-use commercialized polymer from H. C. Starck, Inc. The precursor solution of this PEDOT material was spin coated on the wafers and etched by oxygen plasma, which generated a nano-columned structure of the PEDOT film. The etched PEDOT film was stable under ambient environment and showed promising results for humidity detection. The fabrication method is very simple yet cost effective compared with other methods such as vacuum deposition or other non-vacuum techniques. The choice of substrate is also flexible. Any cheap glass, plastics, or metals can be used as a substrate depending on the application. In addition, the nano-columned PEDOT film has the potential for mass production. In this chapter, the fabrication process flow and PEDOT film characterization are described.

4.2 EXPERIMENTAL PROCEDURES

4.2.1 Spin coating of PEDOT

PEDOT (CLEVIOS P) was purchased from H. C. Starck, Inc. CLEVIOS P is a commercially formulated monomer solution including the complex of the Polymer Poly (3,4-ethylenedioxythiophene) and Polystyrenesulfonic acid. The specific properties of CLEVIOS P can be tailored by different formulation; for example, the conductivity can be increased up to 600 S/cm. The attractive properties of CLEVIOS P are its chemical, thermal and UV stability with no health or environmental problems. In addition, it is dispersed in water, which means it is ready to use for in-situ polymerization. The lowest conductivity of CLEVIOS P, called CLEVIOS CPUD2, was purchased for this work
studying chemiresistive sensor applications. This formulation is a ready-to-use, lower conductivity coating formulation containing PEDOT:PSS, organic solvents, and polymeric binders. The surface resistivity of a 25 μm thick wet film of this material is $8.8 \times 10^5$ to $1 \times 10^8$ ohm/sq.

To explore PEDOT:PSS sensors, silicon wafers containing four embedded platinum electrodes were used for the substrate. This substrate is exactly the same as the one used for the PANI nanowires’ application. Therefore, the fabrication process of electrodes will be omitted in this chapter.

Acetone and IPA were utilized to clean the wafers, and then the substrate was subjected to a further oxygen plasma clean for 5 min in order to remove any residue or organics remaining on the surface. CLEVIOS CPU2D was spin coated on the 4-inch wafer at 500 RPM for 10 min until polymerization was complete. The color of precursor solution was dark brown before polymerization, but it changed to light purple or brown after coating. Depending on the wafer size, the amount of CLEVIOS CPU2D dispensed onto the wafer varied; hence, the polymerization time is also varied. After spin coating, the wafers were baked at 120 °C for 10 min in a furnace to remove the solvent. Figure 4-1 shows CLEVIOS CPU2D deposited on the electrodes, where the space between electrodes is 10 microns each. It was observed that the color of film was not uniform over the entire wafer. It is likely this is due to the low speed of spin coating and viscosity of precursor solution.
4.2.2 Oxygen plasma etching of PEDOT

Since spin coated PEDOT is chemically and mechanically very stable, direct dry etching could be used to obtain the nano-columned structure of PEDOT via chemical reaction with a mono-atomic reactive species. Generally, oxygen plasmas aggressively attack organic materials and can also increase the temperature of the film. Therefore, the key to generating the nano-coulmned structure is to choose an etching recipe that will only partially etch the PEDOT.

In semiconductor manufacturing, oxygen plasmas are used for removing the photoresist from an etched wafer. In the plasma, a mono-atomic reactive species is generated and this reactive species combines with the photoresist to form what is termed ash and that is removed with a vacuum pump.

Figure 4-1: An optical microscopy image of spin coated PEDOT on the electrodes at 100X resolution.
Because of the well-known effective use of oxygen plasma to etch polymers, we choose the approach to etch PEDOT:PSS. The key factors to make nano-columned PEDOT film by means of oxygen plasma etching is etch time and processing temperature. In order to maintain the small amount of PEDOT as a nano-columned structured thin film on the wafer, it is necessary to keep the temperature of the sample as low as possible during oxygen plasma etching at fixed processing time. A Plasma Therm 720 was used for dry etching the sample, but this system has no sample cooling system (e.g., Helium gas cooling under the substrate). A thermal release tape double sided (Nitto Denko America, Inc) was adopted to mitigate against this heating issue by using it to give better thermal contact to the substrate holder. Figure 4-2 shows the illustration of this tape.

Figure 4-2: The illustration of thermal release tape from Nitto Denko America, Inc.
This tape not only has a thermal sink function, but also excellent adhesion and easy release. The sample was attached with this tape (double coated type) and was loaded into the Plasma Therm 720 and etched under the following process conditions: 50 sccm of oxygen, 50 mTorr of pressure, 160 V of DC bias in the chamber, and 5 min etch time. This process has previously been used to descum resist in the Plasma Therm 720. This was used as a starting recipe. The different etching time for this process was required after examining the surface roughness of samples with an AFM.

4.3 CHARACTERIZATION OF NANO-COLUMNED PEDOT

In order to examine the etching effect, 3 min, 4 min, and 5 min etched samples were characterized by optical microscopy, atomic force microscopy, and electrical I-V measurements.

4.3.1 Optical microscopy

Figure 4-3 shows the optical microscopy image of 3 min etched sample at 100X resolution. The substrate was same with that of PANI nanowire where four platinum electrodes were embedded. The spaces between electrodes are 10 microns and widths of electrodes are 5 microns. After 3 min of etching, there is no big change compared with Figure 4-1 except a color change. The color of the etched samples looked more faded and uniform. It appeared that after 3 min of etching, the PEDOT film was uniformly etched and maintained complete surface coverage over the entire substrate.
Figure 4-3: The optical microscopy image of a 3 min etched PEDOT film on the substrate.

Figure 4-4 shows the optical microscopy image of a 4 min etched sample at 100X resolution. In this case, the color of PEDOT looks more faded and is closer to the color of wafer. It seems that the film do not uniformly cover the electrodes, because there is color change. The film thickness is non-uniform on the substrate.

Figure 4-4: The optical microscopy image of a 4 min etched PEDOT film on the substrate.
Figure 4-5 shows the optical microscopy image of a 5 min etched sample at 100X resolution. The film was partially etched through to the substrate; hence, an islands-like film was formed over the electrodes. Of three different etching times (3 min, 4 min, and 5 min) used, it is not obvious from the optical microscopy images which etching time is the best for generating nano-columned structure. When the etching time was over 5 min, the whole film was etched away. Therefore, 5 min is the maximum etching time used here.

Figure 4-5: The optical microscopy image of a 5 min etched PEDOT film on the substrate.
4.3.2 Atomic force microscopy

Since optical microscopy images could not tell the surface morphology of etched samples, AFM (Atomic force microscopy) was used to determine the optimum etching time for generating nano-columned structure. The scanning range of the AFM tip was 10 microns by 10 microns. This scan range covered the space between electrodes. Figure 4-6 shows the 3D AFM image of the 3 min etched sample. The sample’s surface is very rough with the column-like features with heights around 18 nm.

Figure 4-6: The 3D AFM image of the 3 min etched sample.

Figure 4-7 shows the 3D AFM image of the 4 min etched sample. In this case, most of column-like features are broken down due to longer time of etching. Therefore,
the sample’s surface looks less rough when compared to Figure 4-6. The average height of the features is similar with that of Figure 4-6.

Figure 4-7: The 3D AFM image of the 4 min etched sample.

Figure 4-8 shows the 3D AFM image of the 5 min etched sample. The surface is much rougher compared to Figure 4-7, and higher and sharper column-like features are apparent again. It seems that this etching time is enough to partially etch the film through to the substrate, which causes isolated nano-columned structures to form on the substrate. The height of features is around 30 nm as shown in Figure 4-8. Nano-columned structures shown in Figure 4-6 and 4-8 look promising for sensor applications, because
those structures have larger surface area to volume ratios compared to plain thin films. It is interesting that the structure shown in Figure 4-8 could be used as an open circuit configuration, because the nano-sized voids between nano-columns would work for active sensing areas.

Figure 4-8: The 3D AFM image of the 5 min etched sample.

4.3.3 I-V measurements

The purpose of I-V measurements in this section is to characterize the electrical contacts to the etched PEDOT samples, since the resistivity data of PEDOT was already provided from H. C. Starck Inc. The surface resistance varies from $8.8 \times 10^5$ to $1 \times 10^8$ ohm/sq depending on film’s thickness. The characterization of the 3 min etched sample
was undertaken on a probe station using an HP 4156 semiconductor parameter analyzer at room temperature. There are four platinum electrodes on the substrate that are separated by 10 microns each. I-V measurements were carried out between electrodes 1 & 2, 1 & 3, and 1 & 4. Figure 4-9 shows the results of the I-V measurements. These results show that the etched PEDOT on the electrodes was well contacted with electrodes on the substrate, because there are no voltage drops during sweeping, and the values are proportional to the space between electrodes.

![Graph showing I-V measurements of 3 min etched PEDOT in terms of electrodes 1 & 2, 1 & 3, and 1 & 4 on the substrate.](image)

Figure 4-9: I-V measurements of 3 min etched PEDOT in terms of electrodes 1 & 2, 1 & 3, and 1 & 4 on the substrate.

In the case of the 4 min and 5 min etched samples, the I-V measurements showed a reproducible, non-linear response and like that in Figure 8. This is because PEDOT was partially etched away somewhere on the electrodes. The results are matched with the
previous characterizations such as optical microscopy and AFM where the PEDOT film was partial etched away.

4.4 SUMMARY

Nano-columned PEDOT (CLEVIOS P®) films were fabricated as an alternative way to increase the surface area to volume ratio. PEDOT was spin-coated on a wafer embedded with electrodes and followed by oxygen plasma etching, which generated a nano-columned PEDOT film. The fabrication process is very simple yet cost effective compared to vacuum techniques used to synthesize nano-columned structures. The key factors to making nano-columned PEDOT films by oxygen plasma etching are etching time and processing temperature. In order to maintain the small amount of PEDOT as a nano-columned thin film on the wafer, it is necessary to keep the temperature of the sample as low as possible during oxygen plasma etching. A Plasma Therm 720 (NanoFab) was used for dry etching the samples, but this system had no sample cooling system. A thermal release tape, double sided (Nitto Denko America, Inc), was used to mitigate against the heating issue. This tape not only has a thermal conduction function, but also excellent adhesion and easy release. In order to find a proper etch recipe, the samples were etched at different times: 3 min, 4 min, and 5 min. After characterization by AFM, it turned out that 3 min and 5 min etched samples looked promising for sensing applications. The 3 min etched samples showed nano-columned structure with good electrical contact, while 5 min etched sample showed higher and sharper nano-columned structures which formed a discontinuous film.
4.5 REFERENCES


Chapter 5

APPLICATION TO HUMIDITY SENSING

5.1 DETECTION OF HUMIDITY

Chemiresistive type of PANI nanowire and nano-columned PEDOT sensors were tested for detecting humidity. In this chapter, we will discuss how their unique geometrical features (high surface area to volume ratios) enhance sensing performances of humidity. In addition, other environmental factors such as different temperatures, gases, and long-term stability of sensors are tested.

5.1.1 Measurement system

The humidity detection was carried using the system illustrated in Figure 5-1 which was designed and built for this research. This system could control the humidity and temperature independently; relative humidity could be modulated from 18% to 95% at constant temperature. High purity nitrogen gas was used for both a moisture carrier and a purging gas. A ball-flow meter and three valves controlled the gas flow and moisture of the system. Moisture was introduced into the chamber when V1 and V3 are opened, and V2 is closed, purging the chamber is vice versa.
A glass chamber was custom built at Penn State glass shop, with two inlets and two outlets. The first inlet was used for purging, and the other inlet was connected with a bubbler to introduce moisture into the chamber. The temperature of the moisture was also controlled by coiled tube wrapped with heating tape. The first outlet was used for gas exhaustion in order to maintain the ambient pressure inside the chamber, and the other outlet was used as a feed-through for electrical connections. Constant temperature and pressure are crucial experimental factors for precisely detecting humidity, since the relative humidity of an air-water mixture is defined as the ratio of the partial pressure of water vapor in the mixture to the saturated vapor pressure of water at a given temperature. Relative humidity is expressed as Equation 5-1. A percentage of RH is calculated in the following manner:
RH = \frac{P(H_2O)}{P^*(H_2O)} \times 100\% \tag{5-1}

where:

RH is the relative humidity of the mixture being considered, P(H_2O) is the partial pressure of water vapor in the mixture, and P^*(H_2O) is the saturation vapor pressure of water at the temperature of the mixture.

A sample holder was made of Teflon® customized at the Penn State machine shop, and two stainless holder clips which are adjustable depending on the sample size. There are no corrosion issues inside of the chamber that may cause contamination during humidity measurements. In addition, a reference sensor (Thermo & Hygro sensor, Oregon®, USA) was placed inside of the chamber to monitor the temperature and relative humidity simultaneously. The sample’s voltage and current were monitored by a pico-ampere meter / DC voltage source (HP4140B) and collected by a computer through HP-IB interface.

5.1.2 Application of polyaniline (PANI) nanowires to humidity sensing

Two different widths of PANI wires were tested for detecting humidity: 10 \, \mu m and 200 \, nm. The length of both the wires was 5 \, \mu m and the height 200 \, nm. The key to the characterization was to verify the surface volume ratio effect by comparing the PANI nanowire with micron scale PANI wire. In addition, other environmental factors that might affect the performance of humidity detection such as temperature, other gases, and long-term stability will be discussed.
5.1.2.1 Mechanism of interaction between moisture and the polyaniline (PANI) nanowire

Polyaniline and its derivatives have been known to be humidity sensitive for a long time [1]. Depending on the oxidation state of PANI, the PANI structure contains two basic forms: non-oxidized (reduced) and oxidized structures (Figure 5-2). Due to the un-bonded electron pair on the nitrogen atom, both forms can be protonated: -NH- $\rightarrow$ -NH$_2^+$ and -N= $\rightarrow$ -NH$^+$= . According to a buildup model [1], the electron transfer (hopping) from the protonated reduced form (-NH$_2^+$-) to the protonated oxidized form (-NH$^+$=) is the dominant conduction process of PANI when the water content reaches 0.1% (mole ratio). Since in this process a proton is transferred to water by the reaction, -NH$_2^+$- + H$_2$O $\rightarrow$ -NH$^+$= + H$_3$O$^+$, absorbed water plays an important role in the conductivity. The humidity sensing property of PANI to water vapor can be regarded as an electron hopping assisted by proton exchange [2].

Figure 5-2: Two redox forms of polyaniline [1].

5.1.2.2 Impact of structure: surface to volume ratio effect

It has been known that a high surface to volume ratio is a key to effective resistive sensor structures, which improves detection sensitivity and response time since it
provides more reaction area for target species adsorption or absorption, and reduces diffusion time [3]. However, there are a few reports on the sensing performance of single conducting polymer nanowire due to the difficulties of preparing such a sensor [4]. In addition, there are no reports to directly compare the humidity sensing performance between thin films and nanowire PANI. This was done in this work. PANI nanowires and wires were fabricated under the same processes and tested under following conditions: 1V bias was applied to the anode, temperature was fixed at 23°C, and relative humidity range was varied from 25% to 80%. Figure 5-3 shows the percentage changes of current of each wire at different relative humidity conditions. As the surface to volume ratio increases about three times, the detection sensitivity increases about twice. This is the first comparison of surface to volume ratio effect for a single PANI nanowire known to exist.
5.1.2.3 Influence of temperature

PANI has been reported as one of the most environmentally stable materials among conducting polymers [5]. However, this is true mainly in its non-conducting form, emeraldine base, while the more interesting conducting form, protonated emeraldine salt, is much less stable [6]. The degradation of the electrical conductivity in ambient environmental conditions is an undesirable phenomenon for sensing applications. This problem can be related to both intrinsic and external factors. The former are related to polymer structure through the perfection of quinoid and benzenoid unit repetition, the chain ordering, and the dopant selection. The latter are linked to the conditions of the tests through the effect of the environment such as temperature, humidity, and UV light.

Simplifying external factors is necessary for understanding the degradation mechanism. In order to obtain a simplified environment, the humidity was fixed and the

Figure 5-3: Percentage changes of current of each wire at different relative humidity conditions.
sample was excluded from UV light. The environmental chamber (ESPEC SH-241H, temperature range -40°C to 150°C, humidity range 30% to 95% RH) shown in Figure 5-4 was used for testing the sensor response. This set-up has a wider range of temperature control compared to the humidity detection set-up shown Figure 8. In addition, this chamber was totally sealed from the outside environment: there was no light source to affect humidity measurement. The humidity was set to RH 75% and the temperature swept from 12°C to 35°C. According to the literature, RH 75% was supposed to be enough to protonate the PANI nanowires, and increase the measured current. However, the current of 200nm PANI nanowire quickly decayed when temperature was over 25°C as shown Figure 5-5.

![Environmental Chamber Diagram](image)

Figure 5-4: Illustration of environmental chamber set-up.
The decline in electricrical conductivity of the polyaniline nanowire appears to be a result of the combination of these factors (loss of conjugation, chain degradation, deprotonation, oxidation, and crosslinking), which can interact through different mechanisms [7]. However, the mechanisms are not clearly understood yet. A cause for this can be the intrinsic material’s properties dependence on temperature, or the solution degraded. To check on the latter, a new aniline monomer solution (0.3 M aniline monomer and 1M HCl) was prepared, and a re-synthesized 200 nm PANI nanowire was tested under same experimental conditions; however, the result was similar with the previous case. Another possibility for degradation is that residue containing inhibitors may remain or interact with molecular structure after polymerization. Generally, the molecules of these monomers almost always have double bonds (-C=C-), which are very

Figure 5-5: Temperature versus current of 200nm PANI nanowire at RH 75%.
susceptible to half-breaking-open and cross-linking to other molecules in the bottle [8]. When one double bond breaks open, one of its dangling ends attaches to another double bond, making it break too. Some monomer would degrade in one month due to this phenomenon, so the makers add ~0.1% inhibitors to the monomer to increase the life of the bottle to a half-year or more. Inhibitors occasional attach themselves to the dangling bond ends before they can find another double bond to link with, so the chain-reaction is stopped wherever it tries to start. The aniline monomer used here was purchased from Sigma Aldrich® and has 99.5% purity and 0.03% nitrobenzene (C₆H₅NO₂) with water. Nitrobenzene is not an inhibitor and there is no information as to what kind of inhibitors they used. In order to investigate the effect of inhibitors, distillation of the aniline monomer was done at 135 °C, and a high purity of aniline monomer was obtained. Distilled aniline monomer was kept at a brown bottle wrapped with aluminum foil due to its light sensitivity. The distilled monomer solution was prepared again (0.3 M aniline and 1 M HCl) and 200 nm PANI nanowires were again synthesized. The sample was tested again under the same experimental conditions. Figure 5-6 shows the change in current of the distilled polyaniline nanowire from 12°C to 35°C at fixed RH 75%.
The current still decreased, but not as rapidly. This behavior matched that measured by Pinto et al [9]. The conductivity temperature dependence for this sample and Pinto et al’s is well described by Equation 5-2 [10].

\[
\sigma^{-1} = \rho_n \exp(-T_m/T) + \rho_0 \exp\left(\frac{-T_0}{T}\right)^{1/2}
\]  (5-2)

where \(\rho_n\), \(\rho_0\), \(T_m\), and \(T_0\) are constants. The first term represents quasi-1D metallic conduction along polymer chains, with \(T_m\) corresponding to the energy of the wave vector, while the second term corresponds to one-dimensional hopping between localized states or tunneling between small metallic islands. The second term will be dominant as the temperature is increased. Also, the value of constant \(T_0\) will be changed depending

Figure 5-6: Temperature versus current of re-synthesized 200 nm PANI nanowire at RH 75%.
on the type of conducting polymer being measured. In the case of PANI, $T_o$ is decreasing as temperature increases.

5.1.2.4 Influence of other gases (CO and H₂)

In order to characterize the influence of other gases under specific humidity conditions, the set-up shown in Figure 5-1 was modified to Figure 5-7 where two other gases, four moisture traps, and a vacuum pump were additionally connected to the system.

![Figure 5-7: An illustration of the gas detection set-up.](image_url)
Two ball flow meters were used to control the amount of analyte gases and nitrogen in the gas mixture. It is important to minimize the humidity in the chamber during the gas detection. Therefore, four moisture traps surrounding the chamber were used to prevent any unwanted moisture from outside of the chamber from entering. Additionally, a vacuum pump with nitrogen purging was used to maintain dry conditions in the chamber. Other configurations of the system are same with Figure 5-1. The customized system is versatile. Because it can be used for detecting humidity and gas individually, also, this system can be operated for detecting gas under controlled humidity condition, or vice versa. We can distinguish which environmental factor is dominating effect on sensing performance during testing the sample in this system.

Carbon monoxide and hydrogen were characterized as analyte gases. Brief descriptions of these gases are as followed. These were chosen as possible interference gases for moisture measurement, because carbon monoxide is one of the most common and dangerous pollutants present in the environment due to emissions from automated vehicles, aircraft, natural gas emission, industrial wastage, sewage leakage, mines, etc. Its poisonous effects on human life are well known. When the level of CO rises beyond the minimum level in the environment, it becomes life threatening and hazardous. Hydrogen is a colorless, odorless and flammable gas. It is recognized as a possible alternative energy source because it burns out clean and may be produced from renewable energy sources. Its small molecular size allows it to penetrate metals and affect their properties, such as strength and durability. Hydrogen has diverse applications in industry: petroleum transportation, cryogenic cooling, semi-conductor manufacturing processes, fuel cell technology, rocket engines and production of chemical substances.
A newly synthesized PANI nanowire sample was loaded into the glass chamber and a vacuum pump was run to reduce the humidity inside of the chamber. When the humidity reached to RH 20 %, the humidity did not decrease further. Therefore, 4 slm of nitrogen was injected to the chamber while the vacuum pump was running, and then the humidity decreased to RH 14 % at 23 °C. A HP 4156 monitored the response to humidity of PANI nanowires in terms of current. The current was saturated at RH 14 % shown in Figure 5-8. In order to characterize the influence of hydrogen at this humidity condition (RH 14 % at 23 °C), the nitrogen valve was closed and a 4 % hydrogen forming gas was injected to the chamber at the same flow rate of nitrogen. The current decreased when the sample was exposed to hydrogen. Nitrogen was again introduced to check the reversibility of the process; however, there was no change in current. This process was repeated, but there was only a minor change of current. The current returned back to its original value both the hydrogen and nitrogen valves were closed. This phenomenon is not clearly understood, because PANI nanowires seem to contain some absorbed moisture, which delays a role in the chemical reaction between PANI and hydrogen. In addition, 50 ppm carbon monoxide was introduced to the chamber after the current had stabilized. It showed results similar to that of hydrogen shown in Figure 5-8.
In order to totally remove moisture from the PANI nanowires, the sample was placed in the chamber and nitrogen was injected at low flow rate (1 slm) for overnight, and then tested again. The humidity condition of the chamber was RH 14 % at 23 °C. Figure 5-9 shows the result of this experiment. The result is completely different under these conditions. There are four peaks the first and second peaks are the response to hydrogen, and the other two peaks are the response to carbon monoxide. There is no selectivity between hydrogen and carbon monoxide; however, the trend of the response is in accorded with reports in the literature [11-12]; i.e., both hydrogen and carbon monoxide increase the current of PANI nanowires when they reacted with PANI nanowires. In addition, the first peak shows greater and faster response compared with other three peaks. It seems that totally dried PANI nanowires chemically reacted with the first injected hydrogen, and minimized the number of reaction sites for the subsequent gases.
5.1.2.5 Test of long-term stability

Another newly synthesized sample was tested for long-term stability under specific environmental conditions. The environmental chamber (ESPEC SH-241H) was used again. The humidity and temperature was set to RH 50 % and 25 ºC. This environmental condition closely mimics the real environment. Figure 5-10 shows the result of this experiment. The maximum testing time is approximately two hours due to the limitations of the software used to monitor the current. The current of PANI nanowires continually decreased with increasing time. Even though the temperature was fixed, the degradation of PANI nanowires continued.

Figure 5-9: The influence of hydrogen and carbon monoxide after overnight nitrogen dry. Note that first two peaks are response to hydrogen, and the last of two peaks are response to carbon monoxide.
5.1.3 Application of nano-columned Polyethylenedioxythiophene (PEDOT) to humidity sensing

Since PEDOT (CLEVIOS P) was recently developed as a commercial product, there are very limited number of research papers published on this material; especially, applications of the material to humidity detection. The use of PEDOT (CLEVIOS P) for humidity sensing applications using a transistor configuration was first reported by Nilsson et al. [13]. Polyamide fibers coated with PEDOT have also been studied for humidity and temperature sensor applications [14]. In this section, nano-columned PEDOT film is fabricated and applied to a breath sensor application. For medical

Figure 5-10: The test of long-term stability of PANI nanowires at RH 50 % and 25 °C.
breathing sensor applications, accuracy, lifetime, speed of response and contamination of sensors are important. Therefore, it is required to develop one-time use sensors with very low manufacturing costs and sensitive responses to analytes. In this work, nano-columned PEDOT was extensively examined for the potential use in breath sensors and it was compared with a flat PEDOT film. The effects of etch time, temperature, surface treatment, influence of other gases, and long-term stability were all examined in this study.

5.1.3.1 Mechanism of interaction between moisture and nano-columned Polyethylenedioxythiophene (PEDOT)

A 3 min etched PEDOT:PSS sample was tested for humidity detection using the system shown in Figure 5-7. The response to humidity was examined from RH 25% to RH 90% at 23 °C. A 1V bias was applied to the sample and HP 4156 monitored the change of current. The response to humidity was opposite to that seen for PANI nanowires; i.e., the current was decreased as the humidity increased. However, the current did not decrease any more but actually saturated after 1 min shown in Figure 5-11. The current recovered to the original value when humidity was back to RH 25 %.
The environmental chamber (ESPEC SH-241H) was used again to establish the precise response to humidity. By using this chamber the humidity conditions, 50 %, 60 %, 70 %, 80 %, and 90 % at 23 °C could be applied. RH 50 % is the lowest humidity condition at 23 °C under this system. The sample was loaded into the chamber, exposed to each humidity condition, and the current was monitored until it saturated as shown in Figure 5-12. The level at which the current saturated decreased with increasing humidity.

Figure 5-11: Nano-columned PEDOT’s electrical response to a continuous humidity condition (RH 25 % ~ 90 % at 23 °C).
Figure 5-12: Nano-columned PEDOT’s electrical response to various humidity conditions (RH 50 %, 60 %, 70 %, 80 %, and 90 % at 23 °C).

Figure 5-13 shows that the saturated current values are linear with percentage humidity.

Figure 5-13: The change in current of nano-columned PEDOT thin film versus change in relative humidity.
The humidity sensing mechanism can be explained by the dipole molecular effects of water vapor on polar polymers such as PEDOT [15]. Since the water molecules have a large dipole moment, they contribute to the decrease in effective conductivity of PEDOT polymer material in the presence of humidity. Experimental results obtained on molecularly doped polymers indicate that the presence of dipoles initiate a decrease in effective carrier mobility [16-17].

5.1.3.2 Impact of structure: etching effects

Under ambient conditions, it was found that moisture saturated the surface of the polymer films within a few minutes. Therefore, it was not only hard to distinguish the effects of etching on the PEDOT films for humidity detection, but also difficult to apply the nano-columned PEDOT film as a humidity sensor under continuous changing humidity conditions. However, nano-columned PEDOT showed a very fast response as may be seen in Figure 5-12. If the recovery time was as fast as the response to humidity, nano-columned PEDOT has the potential of a breath sensor. In order to evaluate this, human respiration was simulated. The tube connected to the bubbler shown in Figure 5-7 was positioned 1 inch away from the top of sample in this breathing simulation. The moisture was cycled into the chamber at a rate mimicking human respiration. Moisture was generated from a bubbler where the heater’s temperature was 80 °C and nitrogen (carrier gas)’s flow rate was 4 slm. This setup allowed for injections of moisture at RH 90 % and 26 °C. This humidity level is similar with that of a human’s breath.
Figure 5-14 shows the breath test of an unetched flat PEDOT sample. The response time to humidity was very fast, but exhibited a slow recovery time. Each data point corresponds to a 1 second interval, therefore, we can estimate that the recovery time of an unetched sample is around 7~10 sec. The film does not recover quickly enough for use as a human’s breath sensor. The response and recovery time should be sub-second in order to accurately monitor a human’s breathing pattern. The slow recovery time seems to be related to the surface morphology of sample, since the flat surface should maintain moisture longer compared to nano-columned surface.

Figure 5-14: The breath test of the unetched PEDOT sample.

Figure 5-15 shows the breath test of a 3 min etched sample. Here, one rectangular marker implies 0.7 sec. We can estimate the recovery time is around 1.4 sec. It is
apparent that the 3 min etched sample shows faster recovery time due to its surface morphology.

Figure 5-15: The breath test of the 3 min etched PEDOT sample.

A 4 min etched sample showed a different electrical response to moisture, e.g., the current is increased when moisture is injected to the sample, which is shown in Figure 5-16. As it is mentioned on chapter 4, the surface morphology of the 4 min etched sample showed a relatively smooth surface compared to the 3 min etched sample, but the 4 min etched sample probably had tiny voids in the film due to a longer etching time. This means that the PEDOT film, in certain regions, was etched down to the substrate. Therefore, the reaction between voids and moisture is dominating in this sample rather than the reaction between film and moisture. The response and recovery times of the 4 min etched sample are faster than that of 3 min etched sample. Also, the response has a sharper peak compared with Figure 5-15.
A 5 min etched sample showed results similar to that of the 4 min etched sample, but it has a higher noise level as shown in Figure 5-17. Since the 5 min etched sample has an island like film structure, it spreads out over the electrodes and causes bad electrical contact with electrodes and generates excessive electrical noise. Even though the noise level is high, the response to humidity is still sharp and fast. It is an increase in current with humidity, which supports our data interpretation for Figure 5-16.
Figure 5-17: The breath test of the 5 min etched PEDOT sample.

Figure 5-18 shows the test of a bare electrode under same experimental sequences. As we can see, the noise level is too high to distinguish the response to humidity. This is good reference data to compare with other etched samples and find out the etching effect.

Figure 5-18: The breath test of the bare electrode sample.
5.1.3.3 Surface treatment of PEDOT

Since the solvent of the precursor solution is water, the lifetime of PEDOT breath sensor became an issue. If, for example, the sensor is closely attached under a patient’s nose, a drop of secretion can accidently dissolve the PEDOT film. In order to prevent this accident, covering the film’s surface with protection materials or administering surface treatments to the film would be required.

Since it has been reported that ionic crosslinking of the excess anionic sulfonate groups of PEDOT by bivalent Mg$^{2+}$ or Ca$^{2+}$ ions prevents the polymer coating from disintegrating (as it does in pure water) [18] due to water, it was decided to explore this, 0.25 M CaCl$_2$ was prepared as a solution for crosslinking. There were two PEDOT samples, one was an unetched flat PEDOT film, and the other was a 3 min etched nano-columned PEDOT film. Both samples were soaked in the 0.25 M CaCl$_2$ solution for 1 hour and rinsed under DI water for 20 minutes. This process was repeated 3 times to remove any residue. The crosslinked, unetched sample was etched for 3 min for the breath test. However, the film of the unetched sample was partially delaminated after 3 min of dry etching. On the other hand, the etched film prior to crosslinking was fine. It is not clear why this film delaminated, but it seems that the film’s stress might be related to the crosslinking, i.e., thick film before dry etching is more affected by stress than thin film already dry etched.

Electrical characterization was performed after crosslinking the polymer. Figure 5-19 shows the I-V characterization of a 3 min etched sample before and after crosslinking with CaCl$_2$. There is no big difference even after crosslinking.
The response to humidity was in the same pattern as observed in previous experiments with PEDOT, e.g., the current deceased with increasing humidity level as shown in Figure 5-20. Therefore, the CaCl₂ crosslinking with the etched PEDOT film certainly improved the film’s durability against water without losing its sensitivity to moisture.

Figure 5-19: Electrical characterization of an etched PEDOT film before and after CaCl₂ crosslinking.
5.1.3.4 Influence of temperature

The big advantage of humidity sensors based on conducting polymers is room temperature operation. Most humidity sensors based on oxides typically have to increase and maintain a temperature for precise humidity detection. Operation at room temperature makes the sensor simple, small, and cheap.

Since polymers are sensitive to high temperatures, it is important to determine the maximum operating temperature of the sensor for its reliability. For this experiment, the environmental chamber (ESPEC SH-241H) was used and set to a moderate humidity condition (RH 50 %), the temperature was then varied. The lowest temperature at RH 50 % was 20 °C and the highest temperature was 90 °C. A 3 min etched sample was loaded into the chamber and tested. Figure 5-21 shows the current versus temperature response at fixed RH 50 %. Water molecules start to dynamically act in the chamber as the

![Graph: Current versus temperature response at fixed RH 50%](image)

Figure 5-20: The breath test of the 3 min etched PEDOT sample after CaCl₂ crosslinking.
temperature is increased. Hence, the current keeps decreasing (more responses to humidity) as the temperature increases. Eventually, the film began to degrade at 50 °C as shown in Figure 5-21.

![Graph showing current variations with temperature](image)

Figure 5-21: The influence of temperature at fixed RH 50 %.

5.1.3.5 Influence of other gases

Two environments (4 % of hydrogen and 50 ppm of carbon monoxide) were used to test the influence of gases on the PEDOT:PSS sensor. The experimental procedures and system set-up were exactly same as that of PANI nanowires done in section 5.1.2.4. Figure 5-22 shows the result of this experiment. The current of the 3 min etched nanocolumned PEDOT increased as the humidity decreased inside the chamber. The reference sensor inside the chamber was stabilized at RH 14 % at 23 °C, and then hydrogen and
carbon monoxide were injected into the chamber. Interestingly, this produced no distinct change of current due to the amount of noise level.

Figure 5-22: The influence of hydrogen and carbon monoxide under RH 14 % at 23 °C.

The sample was placed inside the chamber and was dried by nitrogen overnight to exclude the possibility of a moisture effect inside of nano-columned PEDOT. When this is done, the gases had little influence on the response of the sensor as seen in Figure 5-23. The signal-to-noise ratio was very low when the nano-columned PEDOT was exposed to the gases. It seems that nano-columned PEDOT is a relatively chemically inert material when compared to the PANI nanowires. In addition, the increased noise level under low humidity condition appears to be due to small amounts of water adsorbed on the sample’s
surface. Since moisture can not be totally removed from the chamber under the set-up shown in Figure 5-7, small amount of water may still reside on the sample’s surface and may be affected by the gas flow and generate non-uniform moisture coverage on the sample’s surface.

![Figure 5-23](image)

**Figure 5-23:** The influence of hydrogen and carbon monoxide after overnight nitrogen dry.

### 5.1.3.6 Test of long-term stability

The testing of long-term stability was carried using the environmental chamber (ESPEC SH-241H). The environmental condition was same with that of the PANI nanowire tests, i.e., RH 50 % and 25 °C. Nano-colummed PEDOT showed better long-
term stability compared to the PANI nanowires, because the current saturated and did not degrade with additional time as shown in Figure 5-24.

![Figure 5-24: The test of long-term stability of nano-columned PEDOT at RH 50% at 25 °C.](image)

5.2 SUMMARY

We have explored chemiresistive sensors fabricated using nano-scale PANI and PEDOT:PSS. These two conducting polymers, PANI and PEDOT, were synthesized with the PANI as nanowires and PEDOT as a nano-columned film. These polymers were assembled on a substrate containing embedded platinum electrodes. Both the PANI nanowires and nano-columned PEDOT films were tested for humidity detection using a
system designed and built for this work. Electrical current-voltage measurements monitored the change in current, or response, of the sensors to moisture.

One goal of the experiments was done to characterize the surface area to volume ratio effect for detecting moisture, since nanowire and nano-columned structures have larger surface area to volume ratios compared to common thin films. The high surface area to volume ratio makes nano-structured sensors faster and more sensitive to analytes. To explore this, a 200 nm PANI nanowire and 10 μm PANI wire were directly compared for detecting moisture, and it was shown that the PANI nanowire had a higher sensitivity. The same experimental procedure was applied to a comparison of PEDOT and nano-columned PEDOT. Etched PEDOT was used to obtain a nanostructured material but it was difficult to distinguish the etching effect of PEDOT films for humidity detection, it was also difficult to apply nano-columned PEDOT film as a humidity sensor under continuously changing humidity conditions, because the moisture saturated the surface of samples within a few minutes. However, nano-columned PEDOT film showed excellent performance in simulated breath tests. Since polymers are sensitive to heat, it is important to characterize the influence of temperature. PANI nanowires and nano-columned PEDOT were tested in the environmental chamber where the humidity was fixed and only the temperature was varied. In the case of the PANI nanowire, it showed very fast degradation at temperatures greater than room temperature, while the nano-columned PEDOT film was fine until the temperature reached 50 °C. The influence of CO and H₂ was also tested to explore sensitivity, selectivity, and chemical stability. In order to exclude the moisture effect during the measurement, the samples were
characterized under the lowest humidity condition, RH 14%. The PANI nanowires responded to the hydrogen and carbon monoxide, but the moisture inside of PANI nanowire influenced the degree of gas detection. To accomplish this, samples were dried overnight under a nitrogen environment and tested again. In this case, the PANI nanowires respond to CO and H₂, however, there was no selectivity between these gases. The Nano-columned PEDOT film was also tested under the same experimental conditions. It was shown that response to CO and H₂ was below the electrical noise level. Finally, both samples were tested for long-term stability. PANI nanowires showed almost linear degradation, while nano-columned PEDOT was stable over extended periods of time. It seems that the PANI nanowire is more reactive to the environment compared to the nano-columned PEDOT film. The only disadvantage of the nano-columned PEDOT was that it loses its durability when it is directly exposed to water or highly saturated humidity conditions for extended periods of time. A surface treatment of the PEDOT was developed and then enhanced its durability against water without degrading its sensing performance. Nano-columned PEDOT films look promising as breath sensors in pulmonary monitoring, because they have sub-second response times to humidity and excellent chemical and physical stability.
5.3 REFERENCES


Chapter 6

SUMMARY AND FUTURE WORK

6.1 SUMMARY

Nanostructures, such as nanowires, nanocolumns, and nanotubes, have attracted a lot of attention because of their huge potential impact in a variety of applications. For sensor applications, the nanostructures provide high surface area to volume ratios. The high surface area to volume ratio allows more reaction areas between target species and detection materials and also improves the detection sensitivity and response time. The main goal of this research was to develop innovative methods to accomplish the synthesis of nanowires and nano-coulnmed conducting polymers that could be used for humidity detection. To accomplish this, two methods were used. The first one employed the geometric confinement of a temporary nanochannel template to orient, precisely position, and assemble nanowires as they are synthesized. The other approach simply used spin-coating of a polymer onto a substrate, and subsequent oxygen plasma etching to generate a nano-coulnmed polymer thin film. In both cases, 200 nm silicon oxide coated wafers with embedded platinum electrodes were used. The biggest advantage of these two methods is that they are relatively simple and only require a single-step, i.e., synthesizing and positioning procedures are carried out simultaneously. They both also have the potential to be economical yet environmentally safe. There are no extra nano-building materials to discard or create a health hazard in both methods.
Polyaniline (PANI) and Polyethylenedioxythiophene (PEDOT) conducting polymers were the materials chosen for this research, since they have good material properties; i.e., ease of synthesis, environmental stability, and simple doping/dedoping chemistry. PANI was synthesized as nanowires, but great care was taken as some claims have been made that (carcinogenic) products are formed upon the material degradation. PEDOT is more environmentally friendly with good film-forming properties, high conductivity, high visible light transmission, and excellent stability. For these reasons PEDOT was been adopted for the second approach.

The use of a temporary (PDMS) nanochannel template for the fabrication of electrochemically-synthesized arrays of individual PANI nanowires with fully controlled dimensions, positions, alignment, and electrical contacting was accomplished. During PANI growth in the template, the electrodes on the substrate covered with the template were used to drive the electropolymerization in pre-selected regions of the growth-template. After growth, the template was carefully removed from the substrate, and then the fully exposed PANI nanowire arrays were characterized. FESEM and AFM images verified the dimensions of PANI nanowires. In addition, chemical analysis showed the major composition of PANI to be that expected. Two-point and four-point electrical characterization measurements were made to yield the conductivity value of a single PANI nanowire.

Nano-columned PEDOT (CLEVIOS P®) nano-structured films were fabricated as an alternative way to increase the surface area to volume ratios. PEDOT was spin-coated on the wafer embedded with electrodes and followed by oxygen plasma etching. This procedure generated a nano-columned PEDOT film. The fabrication process is very
simple yet cost effective compared to vacuum techniques for synthesizing nano-columned structures. The key factors involved in making a nano-columned PEDOT films by the oxygen plasma etching procedures used here are etching time and processing temperature. In order to maintain the small amount of PEDOT as a nano-columned, thin film on the wafer, it is necessary to keep the temperature of the sample as low as possible during oxygen plasma etching at a fixed time. A Plasma Therm 720 (NanoFab) was used for dry etching the sample, but this system has no sample cooling system. A thermal release tape, double sided (Nitto Denko America, Inc), was used to solve the heating issue. This tape not only has the thermal conduction function, but also has excellent adhesion and easy release. In order to determine a proper etch recipe, the samples were etched at different times: 3 min, 4 min, and 5 min. After characterization with AFM, it was found that 3 min and 5 min etched samples looked promising for sensing applications. 3 min etched samples showed a nano-columned structure with good electrical contact, while the 5 min etched sample showed higher and shaper nano-columned structures with an open circuit configuration.

Both PANI nanowires and nano-columned PEDOT films have been tested for humidity detection in a system designed and assembled as part of this work. The response (current changes) to moisture was electrically monitored. A 200 nm PANI nanowire and 10 μm PANI wire were directly compared for detecting moisture, and it was shown that the PANI nanowire had a better sensitivity. The same experimental procedures could not be applied to the nano-columned PEDOT film, because the moisture saturates the sample surface within a few minutes. Further, it was difficult to distinguish the effects of etching the PEDOT film for humidity detection, and also difficult to apply nano-columned
PEDOT films as a humidity sensors under continuously changing humidity conditions. However, nano-columned PEDOT films showed excellent performance in simulated breath tests.

Since the polymers are sensitive to heat, it was important to characterize the influence of temperature on the sensor performance. PANI nanowires and nano-columned PEDOT were tested in the environmental chamber where the humidity is fixed, and only the temperature was varied. The PANI nanowire showed very fast degradation at temperatures above room temperature, while the nano-columned PEDOT film was fine up to 50 °C. The influence of CO and H₂ gases was also tested to explore sensitivity, selectivity, and chemical stability. In order to exclude moisture effects during the measurement, the samples were characterized under the lowest humidity condition, RH 14 %. The PANI nanowires respond to the gases (hydrogen and carbon monoxide), but the moisture inside of the PANI nanowire influenced the gas detection; therefore, the samples were dried overnight under a nitrogen environment and tested again. This procedure showed that PANI nanowires respond to CO and H₂; however, there is no selectivity between gases. Nano-columned PEDOT films were also tested under the same experimental conditions. It was shown that any response to CO and H₂ was below the electrical noise. Finally, both samples were tested for long-term stability. PANI nanowires showed almost linear degradation, while nano-columned PEDOT was stable over extended periods of time. It seemed that the PANI nanowires were more reactive to the environment compared to the nano-columned PEDOT films. The only disadvantage of the nano-columned PEDOT is that it loses its durability when it is directly exposed to water or highly saturated humidity for long periods of time. A surface treatment of the
PEDOT was explored and forward to enhance its durability against water without degrading its sensor performance. Nano-columned PEDOT films look promising as breath sensors because they have sub-second response times and are very chemically and physically stable.

6.2 FUTURE WORK

The work undertaken in this research included: exploring the growth techniques, characterization, and humidity detection of two nanostructured polymers. It is suggested that future work is needed and it should focus on:

1. Switching the substrate to an inexpensive and flexible material and synthesizing the nano-columned PEDOT film as a breath sensor.
2. Characterizing and testing the humidity detection as a function of the bending of nano-columned PEDOT films.
3. Synthesizing additional polymers and examining their selectivity.
4. Integrating different polymers into a circuit to form an electronic nose.
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Pilyeon Park was born in South Korea, on May 8, 1974. He received the B.S. from the Department of Materials Science and Engineering at Hanyang University, South Korea, in 1999. Pilyeon Park began his graduate studies in the Department of Materials Science and Engineering, the University of Florida, USA, in 2000, and obtained his M.S. in 2001. He continued his Ph.D. work in the Department of Materials Science and Engineering, the Pennsylvania State University, USA, in 2002.

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