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NANOSTRUCTURED ARRAYS FOR SENSING AND ENERGY STORAGE APPLICATIONS

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NANOstructured arrays for sensing and energy Storage applications

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abstract of dissertation

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Raghu Mangu
Lexington, Kentucky

Co-Director: Dr. Vijay Singh, Professor of Electrical Engineering
Co-Director: Dr. Stephen Lipka, Professor of Electrical Engineering
Lexington, Kentucky
2011

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ABSTRACT OF DISSERTATION

NANOSTRUCTURED ARRAYS FOR SENSING AND ENERGY STORAGE APPLICATIONS

Vertically aligned multi walled carbon nanotube (MWCNT) arrays fabricated by xylene pyrolysis in anodized aluminum oxide (AAO) templates without the use of a catalyst, were integrated into a resistive sensor design. The steady state sensitivities as high as 5% and 10% for 100 ppm of NH$_3$ and NO$_2$ respectively at a flow rate of 750 sccm were observed. A study was undertaken to elucidate (i) the dependence of sensitivity on the thickness of amorphous carbon layers, (ii) the effect of UV light on gas desorption characteristics and (iii) the dependence of room temperature sensitivity on different NH$_3$ and NO$_2$ flow rates. An equivalent circuit model was developed to understand the operation and propose design changes for increased sensitivity.

Multi Walled Carbon NanoTubes (MWCNTs) – Polymer composite based hybrid sensors were fabricated and integrated into a resistive sensor design for gas sensing applications. Thin films of MWCNTs were grown onto Si/SiO$_2$ substrates via xylene pyrolysis using chemical vapor deposition technique. Polymers like PEDOT:PSS and Polyaniline (PANI) mixed with various solvents like DMSO, DMF, 2-Propanol and Ethylene Glycol were used to synthesize the composite films. These sensors exhibited excellent response and selectivity at room temperature when exposed to low concentrations (100ppm) of gases like NH$_3$ and NO$_2$. Effect of various solvents on the sensor response imparting selectivity to CNT – Polymer nanocomposites was investigated extensively. Sensitivities as high as 28% was observed for a MWCNT – PEDOT:PSS composite sensor when exposed to 100ppm of NH$_3$ and -29.8% sensitivity for a MWCNT-PANI composite sensor to 100ppm of NO$_2$.

A novel nanostructured electrode design for Li based batteries and electrochemical capacitor applications was developed and tested. High density and highly aligned metal oxide nanowire arrays were fabricated via template assisted electrochemical deposition. Nickel and Molybdenum nanowires fabricated via cathodic deposition process were converted into respective oxides via thermal treatments and were evaluated as electrodes for batteries and capacitor applications via Cyclic Voltammetry (CV). Several chemical baths were formulated for the deposition of
pristine molybdenum nanowires. Superior electrochemical performance of metal (Ni and Mo) oxide nanowires was observed in comparison to the previously reported nanoparticle based electrodes.

**KEYWORDS:** AAO, Multi Walled Carbon Nanotubes, Electrochemical capacitors, Lithium-ion batteries, Gas Sensors

Raghu Mangu

18 August, 2011
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DISSELTATION

Raghu Mangu

The Graduate School
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(DEDICATION)

To my Father
ACKNOWLEDGEMENTS

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CHAPTER 1: INTRODUCTION

Fabrication, characterization and integration of nanostructured arrays into devices for gas sensing and energy storage applications are the main objectives of this dissertation. The review presents an in-depth discussion on Multi Walled Carbon Nano Tubes (MWCNTs) and metal nanowire arrays and their related applications along with an understanding of the underlying concepts and techniques involved.

This discussion focuses on fabrication of inexpensive sensor devices that operate at room temperature, which is a challenging task for researches who are consistently designing ingenious ways to achieve this goal. This includes growth of Carbon nanostructures on two different substrates by Chemical Vapor Deposition (CVD) that form the basis for gas sensing mechanism. The different substrates include silicon and highly ordered free-standing porous alumina membranes (AAO).

Highly ordered anodic aluminum oxide templates were fabricated by a two step anodization process. Vertically aligned multi-walled carbon nanotube (MWCNT) arrays were grown in these templates through xylene pyrolysis, without the use of a catalyst and were integrated into a resistive sensor design. During the xylene pyrolysis, a thin layer of amorphous carbon (5–50 nm), forms on both sides of the template as a by-product of the CVD process. This a-C layer plays a crucial role in determining baseline resistance and the sensitivity, since it affects the current path. A study was undertaken to elucidate (i) the dependence of sensitivity on the thickness of amorphous carbon layers, (ii) the effect of UV light on gas desorption characteristics and (iii) the dependence of room temperature sensitivity on different NH$_3$ and NO$_2$ flow rates. An equivalent circuit model was developed to understand the operation and propose design changes for increased sensitivity.

Thin films of MWCNTs were grown onto Si/SiO$_2$ substrates via xylene pyrolysis using Ferrocene as a catalyst via CVD technique. Polymers like PEDOT:PSS and
Polyaniline (PANI) mixed with various solvents like DMSO, DMF, 2-Propanol and Ethylene Glycol were used to synthesize the composite films. These sensors exhibited excellent response and selectivity at room temperature when exposed to low concentrations (100ppm) of analyte gases like NH$_3$ and NO$_2$. Effect of various solvents on the sensor response imparting selectivity to CNT – Polymer nanocomposites was investigated extensively.

Lithium based batteries and electro chemical capacitors are current power sources of choice for a wide range of applications spanning from portable electronics to automobiles. As part of this research study, high density high aspect ratio novel metal oxide nanostructure arrays were fabricated via electro-chemical synthesis. Ni and Mo oxide nanowires were fabricated via template assisted Electro deposition technique and tested as electrodes for Li based batteries and electro-chemical capacitor applications.

Metal oxide nanowire based electrodes were assembled in a leak proof Swagelok cell with metallic Lithium as a counter electrode and LiPF$_6$ as an active electrolyte. The electrodes were then tested for various electro-chemical characteristics including cyclic voltammetry and galvanostatic cycling. The superior electrochemical performance of metal oxide (Ni and Mo) nanowires in comparison to the previously reported nanoparticle based electrodes can be attributed to its very high surface area and shorter diffusion lengths. Free standing metal oxide nanowires on a metal current collector not only buffers the volume change during cycling but also effectively increases the contact among the anode, current collector and the electrolyte. Also, this structure minimizes the contact resistance between the metal oxide and current collector hence, enhanced kinetics of reactions was observed.

On the other hand, for an electro-chemical capacitor application, these electrodes were tested in a half cell three electrode configuration with saturated calomel and platinum as the reference and counter electrodes respectively in a KOH medium. Electro-chemical properties of Nickel, Nickel oxide, Molybdenum and
Molybdenum oxide nanowire based electrodes were thoroughly evaluated by cyclic voltammograms and galvanostatic charge-discharge in 6 M KOH electrolyte. These electrodes exhibited good capacitive behavior and excellent cyclability.

Structural properties of nanostructures fabricated as part of this research study were thoroughly investigated using various techniques including Scanning Electron Microscopy (SEM), Tunneling Electron Microscopy (TEM), X-Ray Diffraction (XRD), Optical Absorption (UV-Vis), Fourier Transform Infrared Spectroscopy (FTIR) as well as electrical characterization techniques.
CHAPTER 2: RESEARCH OBJECTIVE/STATEMENT OF WORK

The principal objective of this research effort is to develop novel nanostructures for gas sensing and energy storage applications. Nanostructures relevant to the research work mentioned here are MultiWalled Carbon NanoTubes (MWCNTs) and Metal-oxide nanowires (Ni, Mo). Over the course of the period, the principal objective of the research program was accomplished by satisfying the following technical objectives;

- To investigate different device configurations for MWCNT based sensors; MWCNTs embedded inside AAO membranes and MWCNTs on silicon substrates
- To elucidate the dependence of sensitivity on the a-C layer. Inexpensive and efficient etch technique to not only tailor the a-C layer thickness but also functionalize the nanotubes
- To demonstrate the role and significance of conducting polymers in imparting selectivity to CNT-polymer based composite hybrid sensors. Effect of various polymers on the sensor characteristics was thoroughly examined
- To fabricate high density and high aspect ratio metal nanowires including Nickel and Molybdenum via template assisted electrochemical deposition and integrate them as electrodes for Lithium based batteries and electrochemical capacitors
- To thoroughly study the electro-chemical properties of Nickel, Nickel-oxide, Molybdenum and Molybdenum-oxide nanowires via Cyclic Voltammetry and DC galvanic charge-discharge experiments.
3.1. Background

Carbon nanotubes (CNTs) were discovered in 1991 by S. Ijiima [1]. They are molecular-scale one dimension tubes of graphitic carbon with some unique properties and can be divided into two categories, namely the single-walled carbon nanotubes (SWNTs) and the multi-walled nanotubes (MWNTs). An ideal SWNT is a Carbon cylinder made up of a single graphite layer rolled up around one axis, with hemispherical end caps. The main body of a SWNT is made purely of hexagons. The end caps correspond to half a fullerene molecule; hence they are made of hexagons and pentagons. On the other hand, a MWNT is made of coaxial SWNTs where, where each successive outer shell has a larger diameter but retains the characteristic rolled graphene structure, as shown in figure 3.1. Notice that possible interactions between walls may stabilize the nanotube growth.

![Schematic of a MWCNT](image)

**Figure 3.1: Schematic of a MWCNT**
Figure clearly illustrates some of the MWCNTs with varying number of walls, outer nanotube diameters, and inner tube diameters characteristics. The bonding within the CNT walls is covalent [2], while the bonding between CNTs, either in a bundle or between CNTs arranged in a MWNT structure, is Vander Waals.

Figure 3.2: The first electron micrographs to be identified as carbon nanotubes. The images are of MWNTs. In (a) the MWNT has 5 shells and a diameter of 6.7 nm. In (b) the MWNT has 2 shells and a diameter of 5.5 nm. In (c) the MWNT has 7 shells and a diameter of 6.5 nm. (Adapted from S. Iijima, Nature, copyright 1991 Macmillan Magazines, Inc.).

Since their discovery, significant progress has been achieved in both understanding the fundamental properties and exploring possible engineering applications of CNTs [3]. The good conducting features of graphite are found only
partially in CNTs, which turn out to be electronic hybrids. SWNTs are either metallic or semimetallic, depending on the geometry of a graphene sheet rolled up into a tube (diameter and chiral angle) [4–6]. Figure 3.3 illustrates chirality which is represented by a pair of indices \((n;m)\) called the chiral vector. The integers \(n\) and \(m\) denote the number of unit vectors along two the directions in the honeycomb crystal lattice of graphene. If \(m = 0\), the nanotubes are “zigzag” and if \(n = m\), the nanotubes are “armchair”. Otherwise, they are called “chiral”. In a SWNT, if \((n \neq m)\) is multiple of 3, then it is metallic, otherwise it is semiconducting.

![Figure 3.3: Chirality in carbon nanotubes. Imagine the hexagonal lattice being rolled such that the green dot (carbon atom) matches up with another colored atom. Each color (red, blue, black) corresponds to a different structure [7]](image)

Some of the other electrical properties experimentally investigated in CNTs are, e.g., the band structure [8], single charging effects [9], Kondo effect [10], ballistic

The mechanical resistance of CNTs is due to one of the strongest bonds in nature, i.e. the C-C sp3 bonding. Their flexibility allows one to bend CNTs repeatedly up to 90° without breaking or damaging them. The exceptional mechanical properties of CNTs find two different applications: the strengthening of fibers in high-performance composite materials, replacing standard C fibers, kevlar, glass fibers; the probes for scanning tunneling microscopes.

Due to several attractive properties, nanotubes are under investigation towards several applications, including electron field emitters [15], cold cathode flat panel display (FPD) [16], microelectronic devices [17], probes of scanning-type microscopes [18], hydrogen storage materials [19], electrode materials of secondary batteries and capacitors [20], particle channeling through micro and nanostructures [21–25]. In addition, CNT-based gas sensors for methane [26], oxygen [27], carbon dioxide [28], and ammonia [29] detection have been reported. Of these areas, field-emission flat-panel display is the closest to realizing commercial products. Moreover, fabrication methods of generating aligned nanotube films on solid surfaces have been developed in many laboratories making nano-electronic devices a commercial reality in the near future.

In recent times, significant research is done to integrate of CNTs into sensor based devises and also achieve an in-depth understanding of the gas sensing mechanisms. Despite many attractive features, commercial solid state device gas sensors do have some drawbacks which impede their performance. The common problems of the solid state devise gas sensors are stability, reproducibility, selectivity and sensitivity. However, the objective of this research was to overcome one of the major disadvantages of gas sensors, i.e., sensing at elevated temperatures. Most of the commercial solid state sensor devices are operated at temperatures ranging from 200°C
to 600°C thus, requiring them to have an in-built heater. This increases the power consumption, weight and the design complexity of the sensor device.

The gas sensing applications of carbon nanotubes in particular is very attractive. CNT-based sensors have been investigated for the detection of gases of H₂, NO₂, CO₂, O₂ and NH₃ [30–35] as well as of other chemicals like organic compounds [36, 37]. Both single wall carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) have been used as the sensing materials. Due to their hollow centre, small size, high surface area, excellent mechanical and electronic properties, CNTs are ideal for gas sensing applications. CNT sensors are also sensitive to low vapor pressure species such as nerve agents, blister agent and explosives, species that are difficult to sense with conventional sensors [38].

As part of this research, we fabricate MWCNTs embedded inside porous alumina membranes which provide a platform for accommodating a definite amount of nanotubes with ordered spatial arrangement. This design poses the advantages of high sensitivity, low power consumption, compactness, high yield and low cost for specific applications like in-situ chemical analysis in space and terrestrial applications. This platform is suitable for detection of gases, chemical analysis in gas phases, and volatile organic compounds.

The sensor devices can be easily transferred from laboratory research scale to mass production due to ability of large-area extensibility of the AAO templates. This integration capability of uniform structure is a key factor in all the device fabrication procedures. Another characteristic of the sensor is the vertical structure, which is contrary to other parallel-to-the-surface structures in that it monitors the gases diffused into the nano pores and adsorbed on the inside wall of the CNTs. We tested the structure as an ammonia sensor using the conductance change upon the gas adsorption. In this device configuration, the MWCNTs are open ended on both sides, which allows the gas molecules to permeate through the tubes and adsorb on the inner walls. Other
researchers have fabricated CNT arrays in AAO templates [39-43]. We are the first group to develop a resistive sensor design based on embedded MWCNTs and obtain high sensitivities to low concentrations of NH\textsubscript{3} and NO\textsubscript{2} gases.

3.2. Research problem

MWCNT based sensor devices are fabricated, either by directly growing nanotubes on substrates via chemical vapor deposition (CVD), or by pasting CNT powders on substrates. In the former method of CNT fabrication, the control over the nanotube growth was difficult to achieve. In particular, the control of the synthesis process is usually not accurate enough to reproduce the length, density and diameter of the CNTs over several operations. On the other hand, in the latter method, the performance and sensitivity of the sensor device is determined by the amount of CNTs in the paste and the type of paste itself. The conductivity and stability of the CNT paste a crucial role in determining the device performance. Also, the content of CNTs in the paste, blending and adhesion of these mixtures onto substrates is a challenge and is yet to be resolved.

Several researchers have reported on the fabrication of CNT arrays and AAO templates [44, 45] Some groups have used an external catalyst particle (Co, Fe or Ni) deposited at the bottom of the AAO template to grow CNT arrays. This method results in the capping of the nanotubes at one end by the catalyst particle which limits the free flow of the gas through the tube as compared to the tubes open at both ends. Also, the chemical purity of the nanotubes can be compromised by the catalyst particles. Also, free standing AAO membranes are fragile and very delicate to operate.

A thin layer of amorphous carbon (a-C) is formed on both sides of the free standing alumina templates as a bi-product of the CVD growth process. The a-C layer provides a conduction path between the metal bus bars involving the aligned nanotubes inside the pores and hence, thickness of this layer plays a crucial role in determining the
device sensitivities. Many groups characterized this layer to be graphene while some report as amorphous carbon. Tailoring the thickness of this thin layer is challenging and novel etching techniques are being explored.

Nanotube arrays exhibited sensitivities to electron-acceptor species such as NO$_2$ and O$_2$ or an electron donor species such as NH$_3$ [46, 47]. Recent reports confirm moisture detection by the nanotube arrays however; lower sensitivities indicate relatively small charge transfer between weakly adsorbed molecules on the surface and the nanotube. Also, CNT sensors require some external agitation like thermal-heat or an electric pulse to desorb the chemisorbed molecules from the surface. On the contrary, higher temperatures may result in a change in the electrical properties of nanotubes while making desorption better.

### 3.3. Experimental Procedures

Porous alumina templates were fabricated by a two-step anodization process of high purity Al tape in a 0.3M oxalic acid medium as reported earlier [48]. The resulting is a free standing 60µm thick high purity aluminum oxide membrane with highly ordered pores open on both sides as shown in figure 3.4

![Figure 3.4: Schematic of a porous AAO template with pores open at both the ends](image-url)
Vertically aligned carbon nanotubes were grown in these templates by chemical vapor deposition (CVD) method. The CVD process was similar to that described previously [49] except that pure xylene was used as hydrocarbon source and a stream of argon/hydrogen was replaced with nitrogen gas. The growth of CNTs in the pores is initiated from the pore walls (the alumina itself acts as a catalyst for CNT growth) and is due to the decomposition of xylene at 700°C. A scanning electron microscope (Hitachi S-900) and transmission electron microscope (JEOL 2010FX) were used for the post-growth characterization of CNTs. AAO templates were dissolved to release CNTs for TEM characterization.

For gas sensing experiments, CNT/AAO arrays with 25 nm CNT inner core diameter and a wall thickness of 5 nm were incorporated into a resistive gas sensor design (figure 3.5), where, contact electrodes (Au bus bars) were deposited by e-beam evaporation technique. A HP 3478A digital multimeter, interfaced with Lab View software, was employed to measure the change in resistance upon exposure to analyte gases. All experiments were carried out at room temperature while, the sensor was placed inside a sealed glass test chamber and the change in the device resistance was monitored as the chamber was cycled between analyte gases and nitrogen. A Sierra Instruments dual channel mass flow controller was employed to control the flow rates of the purging gases and was controlled by LABVIEW interface through a National Instruments USB-6009 Data Acquisition device (DAQ). Nitrogen (N₂) was used as the carrier gas in all experiments and the test gases used included NH₃ and NO₂. Prior to the injection of test gas, the sensor chamber was flushed with nitrogen gas for at least 20 minutes. Using mass flow controllers, the test gas was then injected and the percentage change in resistance (% ΔR/R) of the device was monitored continuously for every 10 min alternate injections of test gas and the carrier gas. A Black-Ray Long Wave Ultraviolet Light Model B 100AP (λ = 365 nm) was used for desorption experiments.
3.4. Results and Discussion

3.4.1. CNT Characteristics

Scanning electron micrograph of figure 3.6(a) shows the top view of the starting AAO template while figures 3.6b and 3.6c show a top view of the AAO template after CNT growth. A layer of amorphous carbon is formed on both top and bottom sides of the free standing porous alumina templates as a by-product of CNT growth process. Thickness of these layers can be tailored through CVD process conditions.
Figure 3.6: (a) AAO tape anodized at 40V; (b) CNTs in AAO with thick amorphous carbon top layer; (c) CNT in AAO with thin amorphous carbon top layer

Transmission electron microscopy observations confirmed that the tubes were open ended and the walls were crystalline, and the wall thickness of the nanotube was 5 nm on either side as shown in figure 3.7. From the TEM observations, the distance between two neighboring fringes was about 3.4 Å, in agreement with the inter-planar separation of graphite (3.35 Å). Also, TEM images showed that the tube walls are smooth with homogeneous thickness. We also investigated the variation of the MWNT diameter with AAO pore diameter. AAO templates of 50 nm, 35 nm, 25 nm and 12 nm pore diameters were prepared and CNTs were grown in them under identical conditions. It was observed that for a fixed growth condition, CNT wall thickness is invariant and the inner core diameter of the CNT decreases proportionately with the AAO pore diameter. All of the CNTs grown in our study were multiwalled in nature and open ended except for the smallest diameter (2 nm) tubes, which were close ended.
Figure 3.7: (a) Transmission electron micrograph of the smallest MWNT grown in AAO; (b) Transmission electron micrograph of the CNT grown in AAO.

3.4.2. Sensor Response

The sensor response was evaluated by measuring the resistance upon exposure to various gases. The sensitivity (S) is defined as,

\[
S(\%) = \frac{R_{\text{gas}} - R_{N_2}}{R_{N_2}} \times 100
\]

(1)

Where \( R_{N_2} \) is the device resistance in the presence of carrier gas \( N_2 \), and \( R_{\text{gas}} \) is the resistance in the presence of test gas.

The effect of amorphous carbon layer thickness on sensitivity of the device was investigated by varying the thickness of amorphous carbon (a-C) layers by tailoring the CVD growth conditions. Figures 3.8 and 3.9 compare the responses of thin and thick a-C layer devices exposed to \( \text{NH}_3 \), a reducing agent. For a device with thin a-C layers (5nm and 30nm on the top and bottom respectively), a baseline resistance of 0.3 M\( \Omega \) and a sensor response of 12% for the first pulse, 5% at steady state, and 20% cumulative, were observed when exposed to 100 ppm of ammonia, as shown in Figure 3.8.
MWCNT-AAO resistive sensors were tested for reproducibility by fabricating four samples under identical conditions and evaluating their sensor response to 100ppm of NH₃ gas. Table 3.1 shows the first pulse, steady state and cumulative sensitivities of these samples along with their error calculations. Also, the average first pulse, steady state and cumulative sensitivities of these samples were plotted with their standard error in a bar graph format as shown in figure 3.9. These results show that the sensor devises exhibited highly reproducible sensitivities.
Table 3.1: Table showing the first pulse, steady state and cumulative sensitivities of four different samples fabricated under identical conditions and tested for reproducibility when exposed to 100ppm NH\textsubscript{3}.

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Average</th>
<th>Std. Dev</th>
<th>Std. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>First pulse</td>
<td>12.2</td>
<td>12</td>
<td>11.6</td>
<td>11.85</td>
<td>12.025</td>
<td>0.252</td>
<td>0.146</td>
</tr>
<tr>
<td>sensitivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steady state</td>
<td>4.6</td>
<td>5</td>
<td>5.2</td>
<td>4.5</td>
<td>4.55</td>
<td>0.330</td>
<td>0.190</td>
</tr>
<tr>
<td>sensitivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cumulative</td>
<td>17</td>
<td>20</td>
<td>21</td>
<td>18.5</td>
<td>17.75</td>
<td>1.75</td>
<td>1.010</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Figure 3.9: A bar graph showing the average values of the first pulse, steady state and cumulative sensitivities of four different MWCNT-AAO resistive sensor samples fabricated under ideal conditions exposed to 100ppm of NH\textsubscript{3}.

Figure 3.10 shows the sensor response of thicker a-C layer device, when exposed to 1% and 5% NH\textsubscript{3}. Sensor response to 5% NH\textsubscript{3} is seen to be 16% for the first pulse, and 9% in...
steady state. For 1% NH$_3$, responses of 6% for the first pulse and 5% in steady state were observed.

![Graph showing sensor response to NH$_3$](image)

**Figure 3.10: Response of CNT/AAO resistive sensor with thicker amorphous carbon at room temperature to 5% NH$_3$ and 1% NH$_3$**

The sensor response of a MWCNT/AAO device to 0.01% NH$_3$ with various a-C layer thicknesses obtained by plasma oxidation technique is shown in figure 3.11. The initial response corresponds to as prepared sample with an a-C layer thickness of 40nm. The Baseline resistance was 2.78 kΩ with 15.37% cumulative sensitivity. Then the sample was subjected to oxygen plasma for 30 sec to decrease the a-C layer thickness to 25nm and the corresponding baseline resistance and the cumulative sensitivity increased to 6.88 kΩ and 16.86% respectively. The sample was further plasma oxidized for another 30 sec and evaluated for its sensor response to 0.01% NH$_3$. The baseline resistance increased to 9.27 kΩ and a cumulative sensitivity of 17.7% was observed. The
increase in baseline resistance and device sensitivity with decreasing a-C layer thickness was observed and is in agreement with the previous experimental results. These results underline the important role played by the amorphous carbon layer as a conducting contact between the adjacent CNTs, even though the primary sensing mechanism involves the interaction of the carbon nanotubes with the analyte. The sensor response to the reducing agent NH$_3$ can be attributed to the charge transfer occurring from NH$_3$ to the MWCNTs as the gas adsorbs on the MWCNT inner surface.

![Graph showing response of CNT/AAO resistive sensor with different a-C layer thickness to 0.01% NH$_3$ at room temperature](image)

**Figure 3.11: Response of CNT/AAO resistive sensor with different a-C layer thickness to 0.01% NH$_3$ at room temperature**

A gradual upward drift of the devise baseline line as time progresses was observed as shown in figures 3.8, 3.9 and 3.10. The reason for this drift can be attributed to the chemisorption of the test gas (ammonia in this case.), which builds up steadily with exposure to each initial pulse containing ammonia; thus higher the ammonia content, higher the upward drift. This would explain the observed fact that
the upward slope of the baseline is higher for the case of 5% ammonia than for the case of 1% ammonia (figure 3.9).

Figure 3.12 shows the response of the thinner layer device when exposed to 100 ppm of NO₂, an oxidizing agent. Responses of 34% for the first pulse, 10% at steady state, and 50% cumulative after 4 cycles were observed. Previous experimental results indicate an increase in conductance of the single walled CNTs when exposed to oxidizing gases like NO₂ [50]. MWCNTs incorporated in our sensor design also show analogous behavior. This behavior may be attributed to the charge transfer occurring from CNTs to NO₂ because of the highly oxidizing nature of NO₂.

Figure 3.12: Response of CNT/AAO resistive sensor with thinner amorphous carbon at room temperature to 0.01% NO₂

MWCNT-AAO resistive sensors were also tested for the reproducibility of their sensor response to 100ppm of NO₂ gas. Table 3.2 shows the first pulse, steady state and cumulative sensitivities of these samples along with their error calculations. Also, the average first pulse, steady state and cumulative sensitivities of these samples were
samples were plotted with their standard error in a bar graph format as shown in figure 3.13. These results show that the sensor devises exhibited highly reproducible sensitivities.

**Table 3.2**: Table showing the first pulse, steady state and cumulative sensitivities of four different samples fabricated under identical conditions and tested for reproducibility when exposed to 100ppm NH₃

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Average</th>
<th>Std. Dev</th>
<th>Std. error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>First pulse sensitivity</strong></td>
<td>33.62</td>
<td>30.81</td>
<td>32.3</td>
<td>34.2</td>
<td>33.91</td>
<td>1.508</td>
<td>0.870</td>
</tr>
<tr>
<td><strong>Steady state sensitivity</strong></td>
<td>12</td>
<td>11.5</td>
<td>12.8</td>
<td>11.4</td>
<td>11.7</td>
<td>0.639</td>
<td>0.369</td>
</tr>
<tr>
<td><strong>Cumulative sensitivity</strong></td>
<td>49.3</td>
<td>46.6</td>
<td>48.2</td>
<td>48.6</td>
<td>48.95</td>
<td>1.144</td>
<td>0.660</td>
</tr>
</tbody>
</table>

**Figure 3.13**: A bar graph showing the average values of the first pulse, steady state and cumulative sensitivities of four different MWCNT-AAO resistive sensor samples fabricated under ideal conditions exposed to 100ppm NO₂
The variation of device resistance in the presence of oxidizing (electron-withdrawing) or reducing (electron donating) gases due to charge transfer between the analytes and the nanotubes suggests that the MWCNTs show a p-type semiconducting behavior. This can be explained as follows. The electrical resistivity of a p-type semiconductor is dominated by holes. The reducing gases like NH\textsubscript{3} donate electrons to the valance band decreasing the number of holes, thereby increasing the separation between the Fermi level and valance band. This results in the formation of a space charge region at the surface of p-type semiconducting CNTs increasing the electrical resistance. Similarly when oxidizing species like NO\textsubscript{2} are adsorbed on the surface of p-type MWCNTs, the Fermi levels are shifted towards the valence band, generating more holes and thus enhancing the conductance.

The electrical response of the resistive sensor indicates a charge transfer between the nanotubes and the gas molecules, and hence, the adsorption of gases on the inner walls of the nanotubes is the dominant sensing mechanism. As the sensor goes through NH\textsubscript{3} – N\textsubscript{2} cycles there is a buildup in chemisorbed NH\textsubscript{3} on the MWCNT surface, which causes an upward drift in the baseline resistance as well as the sensitivity. This is due to the fact that the adsorbate binding energy is sufficiently large and some of the ammonia molecules can be adsorbed at the defect sites available either on the nanotubes surface or on the inner walls of the open ended MWCNTs. The gas molecules adsorbed at these defect sites are hard to desorb. Hence, weakly bonded, physisorbed, molecules desorb with each cycle, while the more strongly bonded (chemisorbed or physisorbed at the defect sites) molecules remain during cycling. Binding energy is high enough that heat or ultraviolet light is needed to desorb the analyte and bring the MWCNTs back to its initial conducting state [51].

Experiments were carried out to study the effect of UV radiation on the recovery of the device baseline resistance by investigating desorption characteristics as shown in figure 3.14. The sensor resistance fell steeply when UV light was used in combination with the carrier gas (N\textsubscript{2}) during desorption cycle, which indicates that the strongly
bonded analyte molecules can be completely desorbed by using high energy UV source, improving the desorption profile without any shift in the baseline resistance after the initial exposure. The recovery process is crucial for practical applications. Our recovery process is relatively simple which requires only the application of a relatively high energy UV light for a short period.

A detailed study was conducted on the dependence of device sensitivity on flow rate of the test gas (NH$_3$) as shown in figure 3.15. The sensitivity was found to increase with an increase in flow rate of the test gas up to 750 sccm and then decreased for 1000 sccm. The device sensitivity was highest for a flow rate of 750 sccm.

Figure 3.14: Sensor response of CNT/AAO resistive sensor with different mechanisms to desorb 0.01% NH$_3$
Figure 3.15: Sensor response of CNT/AAO resistive sensor with different flow rates of 0.01% NH₃

The variation of device sensitivity with flow rate can be interpreted as follows. A change in device resistance occurs when the analyte gas species adsorb on the nanotubes. A flow of N₂ desorbs some species from the surface during N₂ cycles. Therefore, the flow rate is responsible for both the supply of species to the surface and desorption of physisorbed species from the surface. Therefore when the sensor is exposed to an analyte gas (100 ppm NH₃ in N₂), both adsorption and desorption are taking place. The sensitivity increases as a function of flow rate up to 750 sccm. This can be understood as the mass transport limited regime, where an increased flow rate provides an increase of species to adsorb, resulting in an increased sensitivity. The increased flow of the analyte at higher flow rates (1000 sccm), promotes desorption, thus impacting the equilibrium concentration of adsorbed species even with an increase in the available species. The desorption characteristic of the flow-rate is important in
understanding this behavior. If the gas flow didn’t promote desorption, we would expect two regimes: mass transport limited and surface limited, with the latter showing no change in sensitivity with respect to flow rate.

Our sensor results are in agreement with those reported by Bekyarova et al [52] using SWNT-PABS composites. They reported a 22% increase in the resistance of SWNT-PABS composite when exposed to 100ppm ammonia; Kong et al [50] observed an initial increase in resistance of about 30% when their single walled carbon nanotube (SWCNT) sensor was first exposed to 1% ammonia for 1000 seconds. Kong et al. demonstrated that NH$_3$ increases resistance of p-type SWCNTs and NO$_2$ decreases the resistance of p-type semiconducting SWCNT’s [50]. Kong et al. also showed the effect of the analytes remaining on the SWCNT’s after exposure.

Desorption with heat and ultraviolet light are often employed to bring CNT sensors back to initial conditions [51]. Our thinner a-C layer sample showed greater sensitivity for NO$_2$ (100ppm) compared to NH$_3$ (100ppm). This validates the charge transfer based sensing mechanism, as reported by Star et al [53] that NH$_3$ adsorbates donate approximately 0.04 e\textsuperscript{-} per molecule while NO$_2$ withdraw approximately 0.1 e\textsuperscript{-} per molecule.

### 3.5. Equivalent Resistance Model

An equivalent circuit model was developed (as shown in figure 3.16) to understand the operation, and propose design changes for increased sensitivity. The device is understood in terms of the splitting of current between the top a-C layer and an alternate path which includes the MWCNT’s. Additionally, the model enables a current mapping which illustrates the importance of having active MWCNT’s in the circuit. The following model is presented, considering three resistances:
- $R_1$: the resistance of the amorphous carbon (top) between two adjacent MWCNT's
- $R_2$: the resistance of one MWCNT
- $R_3$: the resistance of the amorphous carbon (bottom) between two adjacent MWCNT's

**Figure 3.16: Schematic of the equivalent circuit of one row of MWCNTs**

The methodology adopted is to first calculate the equivalent circuit resistance of one row of CNT’s between the electrodes and then extend it to calculate the total device resistance by considering the number of rows (CNTs) to be in parallel. The number of CNTs was estimated from high resolution electron microscopy images of the CNT/AAO templates. We have observed from our experimental data that the total resistance of the sensor can be changed by changing the thickness of the conducting amorphous carbon layers. This can be achieved by tuning the CVD conditions or by post growth processing. Hence this model incorporates $R_1$ and $R_3$ as the resistance of the top and bottom amorphous carbon layers respectively.

**3.5.1. Equivalent Row Resistance**

Figure 3.14 shows a schematic of one row of MWCNT’s from contact to contact. $\Delta$ to $Y$ transformations was carried out across the row. The equivalent resistance of one row is shown in equation 1. The first term is the initial $\Delta$ to $Y$ transformation. The second term is a summation of all transformations along the row, where $N_x$ is the number of CNT’s in the row.
Each $R_{1i}$ and $R_{2i}$ terms are of the form:

$$R_{1,2i} = \frac{R_2}{R_2 + \left( R_1 + R_{(i-1),1} \right) + \left( R_3 + R_{(i-1)2} \right)} \quad \text{........ (2)}$$

The device resistance $R_{\text{device}}$ is given by:

$$\frac{1}{R_{\text{Device}}} = \sum_{i=1}^{N_y} \frac{1}{R_{Row}} \quad \text{........ (3)}$$

Where $N_y$ is the number of MWCNT’s in the y-direction.

3.5.2. Amorphous carbon resistances $R_{\text{TOP}}$ and $R_{\text{BOT}}$

The top and bottom layer amorphous carbon resistances, $R_{\text{TOP}}$ and $R_{\text{BOT}}$, are calculated taking into account the regions where the amorphous carbon does not cover the open pores. Figure 3.17 shows the shaded region of the conducting path between adjacent MWCNT’s, and the variables used for the calculation in equation 4.
\[ R_{TOP,BOT} = 2 \left( \frac{\rho_{ac}}{2t_{acTOP,BOT}} \int_{\theta=0}^{\pi/2} \sin \theta d\theta \right) \left( \frac{L_1}{2} - r_0 \sin \theta \right) \left( \frac{L_1}{2} - r_0 \right) + \frac{\rho_{ac} L_1}{t_{acTOP,BOT} L_1} \right) \ldots (4) \]

Figure 3.17: Diagram showing conducting path between two adjacent MWCNT’s. The pore is not covered and thus this area is left out of the calculation of \( R_{TOP,BOT} \). \( L_1 \) is pore pitch in x and y directions, \( r_0 \) is the pore radius. \( \theta \) is the angle from x-axis inside the pore used in equation-4.

For the standard templates used in this study, \( L_1=85 \) nm and \( r_0 =20 \) nm. For these dimensions the above expression reduces to equation 5.

\[ R_{TOP,BOT} = \frac{\rho_{ac}}{t_{acTOP,BOT}} \times 1.29 \ldots (5) \]
3.5.3. MWCNT Resistance, $R_{CNT}$

The resistance of the carbon nanotubes is calculated in the following way.

$$R_{CNT} = \frac{\rho_{CNT} h_{CNT}}{\pi \left( \frac{d_{o}^2 - d_{i}^2}{4} \right)}$$      

...... (6)

Where, $\rho_{CNT}$ is resistivity of the CNT’s, $h_{CNT}$ is the height of the CNT’s, $d_{o}$ and $d_{i}$ are the CNT’s inner and outer diameters.

With $R_{ROW}$ calculated from successive $\Delta$ to $Y$ transformations along a single row of $N_{x}$ MWCNTs and $R_{DEVICE}$ calculated as the parallel circuit of $N_{Y}$ Rows, plots can be generated to study device operation.

3.6. Conclusions

Highly ordered porous alumina membranes were fabricated by a two step anodization technique. These templates were used to grow vertically aligned Multi walled carbon nanotubes (CNTs) grown by chemical vapor deposition inside the pores without the use of catalyst and were integrated into sensor designs for detecting NH$_{3}$ and NO$_{2}$ at room temperatures. The fabrication process of these resistive sensors is simple and does not require any special fabrication techniques like e-beam lithography nor photo-lithography. The sensitivity was calculated by the change in resistance of the device when exposed to alternate cycles of carrier and analyte gases. These sensors were responsive to both oxidizing and reducing species at room temperature and a detailed study was conducted on the dependence of sensitivity on the thickness of amorphous carbon layer on both top and bottom.
Thickness of the a-C layer was also varied from 40nm to 25nm and further decreased to 5nm by post growth processing using plasma oxidation technique. The cumulative sensor response to 0.01% NH$_3$ was increased from 15.37% to 16.86% and further increased to 17.7% due to the corresponding decrease in the a-C layer thickness and increase in the baseline resistance. The best response (12% for the first pulse, 5% steady state, and 20% cumulative change) was observed for a sensor with a thin amorphous carbon layer when exposed to 100ppm of ammonia. For sensors with thicker amorphous carbon layer, a 0.7% change for the first pulse and a steady state value of 0.6% change in resistance was observed when exposed to 100 ppm of NH$_3$. The sensors also exhibited an excellent response (a cumulative response of 50% over 4 cycles, an initial response of 34% for the first pulse and a steady state value of 10% change in resistance) to 100 ppm of an oxidizing agent (NO$_2$). The recovery of the device baseline resistance is also simple and only requires application of a high energy UV pulse for a short period.

Changes in the device resistance to different test gases interpreted in terms of a model where the MWCNTs were thought to behave as p-type semiconductors. Charge transfer between the nanotubes and the analyte is an important mechanism in changing the resistance of the sensor when exposed to NH$_3$.

An equivalent circuit model was developed to understand the operation, and propose design changes for increased sensitivity. The device is understood in terms of the splitting of current between the top a-C layer and an alternate path which includes the MWCNT’s. Additionally, the model enables a current mapping which illustrates the importance of having active MWCNT’s in the circuit. This mathematical model developed clearly elucidates the mechanism of resistance change in MWCNTs in MWCNT/AAO resistive sensor devices. The model enables improvements in sensitivity of MWNT based devices and makes their performance on par with the more expensive competitors like SWNT gas-sensing devices.
3.7. Future work

In recent times, there are several research groups developing CNT based sensor devices. The performance, stability and sustainability of these devices can be improved by innovative fabrication techniques and novel device designs. As part of future work of this research, highly ordered porous alumina films on Silicon substrates can be fabricated. AAO films fabricated on Si substrates are mechanically stable and forms regular arrays of nano pores of uniform diameter and length. These samples are easy to handle are robust in nature. Various CVD growth conditions for growing nanotubes inside the pores of AAO film on Si substrates should be investigated. Also, these samples should be integrated into sensors and tested for their sensor characteristics for various gases.

To achieve higher sensitivities to low concentration of gases, the nanotube tips can be modified with various transduction materials [52, 53] like metals and polymers to precisely change the effective adsorption of analyte species and also obtain selectivity. A detail study on the functionalization of nanotubes and their effect on sensor characteristics can be investigated.

To achieve better signal transduction, various electrode configurations as compared to the standard bus bar contacts can be explored. Also, dependence of signal transduction on various metals used as contact materials like Au, Ag, Al and Graphite can be researched.
CHAPTER 4: MWCNTS ON SILICON SUBSTRATES

4.1. Background

Multi wall nanotubes (MWNTs) were discovered by Iijima [54] in a carbonaceous deposit which was a byproduct of a carbon arc process used for producing fullerene. Single wall nanotubes (SWNTs) were discovered in 1993 during the course of synthesizing carbon nano-capsules filled with magnetic fine metal particles (Fe, Co, Ni) [55, 56]. Since, then, a lot of research has been carried out on this novel carbon nanomaterial with much success.

![SWNT and MWNT](image)

Figure 4.1: Schematic diagrams of a SWCNT and MWCNT

Both SWCNTs and MWCNTs as shown in figure 4.1 exhibit unique physical and chemical properties as being a quasi-one dimensional material. The spacing between the nanotubes in a MWNT is examined with TEM and ranges from 0.34 to 0.39 nm, with the spacing changing as the nanotube diameters increase [57], as illustrated in Figure 4.2. Note that the spacing between the shells in the MWNT decreases as the nanotube outer diameter increases and approaches a value of about 0.344 nm at a diameter of
about 10 nm. The larger intershell spacing at smaller nanotube diameters is attributed to the larger repulsive forces associated with the high curvature of the nanotube walls at small diameters.

Figure 4.2. High-resolution transmission electron micrograph of CVD-produced MWNTs clearly showing concentric shell walls and a hollow core. (Courtesy of E.C. Dickey and D. Qian)

CNTs are called zero gap semiconductors because of their unique ballistic conductance property i.e. electrons can travel though the entire length of the nanotube without generating any heat. Also, the conductance properties of nanotubes can be easily varied by simple doping techniques. Hence, due to the exciting electronic properties, CNTs find very novel applications including nanocables or quantum cables, to replace silicon, allowing to go from micro- to nano-electronics; nanodiodes, made by two fused NTs, one conducting and one semiconducting; electron guns for producing plasma screens with ultra-high definition.
The high aspect ratio and large surface area make CNTs ideas for gas absorption. Their ability to exhibit high capillarity makes them suitable for flow membrane and fuel cell applications. Field Emission is a process in which a material emits electrons as result of electric field applied. CNTs have exhibit excellent FE property by emitting high currents, of order 0.1mA by applying a voltage of just a few hundred volts. This property of nanotube, field emission at relatively lower voltages makes it applicable in several areas of industry, including lighting and displays. Electron sources may be industrially the most promising CNTs application, nearly within reach of practical use (for industrial displays the time to market is estimated in two years). Fluorescence occurs when a substance absorbs a light wavelength and emits a different one. CNTs absorb and emit light in the near infrared spectrum. As a potential application of the fluorescence properties of CNTs, a good candidate is provided by NT-based optical biosensors, which might be used to detect specific targets inside the human body, e.g. tumor cells, wrapping the tubes by a protein which can link only to the targeted cells. In conclusion, due to their extreme properties, CNTs are suitable for many applications: electron field emitters, probes of scanning microscopes, hydrogen storage materials, electrodes of batteries, and composite materials for extreme conditions (aerospace environment, large temperature and pressure gradients, radiation and so on). For instance, the high structural perfection, lightweight and chemical inertness of CNTs make them interesting in composite materials for spacecraft atmosphere re-entering applications. Table 4.1 illustrates and summarizes the lifecycle of Carbon nanotubes for potential industrial applications.
Early theoretical studies indicate the Nanotubes as promising intercalation materials for metal atoms[58]. Subsequent studies indicate that nanotubes are easily filled with a variety of elements and compounds such as HNO$_3$, S, Cs, Rb, V$_2$O$_5$, Se, Pb oxides, and Bi oxides.[59] However, when surface tensions are greater than about 100 to 200 mN/m, the material will no longer wet the nanotube walls. Reports show that elements like Te, Pb, Hg and Ga were not able to wet the nanotube surfaces.

Calculations show that transition metal atoms interact differently with nanotubes when compared to graphitic surfaces [60]. Also, large magnetic moments for metal atoms on SWNT walls were observed [60]. 3-d transition metal atoms make a good electrical contact to the nanotubes as they exhibit a very low least electrical resistance when used to form metal-CNT contacts [61]. These details provide the basis for the fabrication of nanometer-scale electronic devices from nanotubes.
Nanotubes exhibit interesting optical characteristics; the helical structures of the SWNTs determine their optical properties with metallic and chiral nanotubes having second-order hyperpolyarizabilities similar to those of conducting polymers [62]. In contrast, when the optical properties of a well-aligned bundle of MWNTs are studied experimentally, and theoretically they are shown to be similar to graphite and are not affected by the helical structure of the MWNTs [63]. Also, the optical properties change slightly with changes in the radii of the MWNTs [63]. An important step toward the use of carbon nanotubes as optical coatings or filters is their incorporation into composite materials. Composites of MWNTs and several different polymer systems have been examined [64]. The results show that the composite materials retain strong nonlinear optical properties, similar to those of MWNT suspensions.

Gas detection instruments are increasingly in demand for industrial health and safety, environmental monitoring, and process control applications. To meet this demand, considerable research into new sensor technologies is underway, including efforts to enhance the performance of traditional devices, such as resistive metal oxide sensors, through Nano Engineering. Recently, it has been demonstrated that CNTs represent a new type of chemical sensor capable of detecting a small concentration of molecules, such as CO, NO₂, NH₃, etc. [65]. Exchange of electrons due to absorption of gas molecules on the CNTs causing a modification of the electrical conductance in the nanotubes, is the basic concept for CNT based sensors. Also, the ballistic electronic transport along the CNT axis provides excellent transmission of the altered electrical signal to the external contact. Third, the long-term performance of CNTs based sensor may be stable due to their chemically robust graphitic surface. CNTs are ideal for gas sensing due to their very high surface area when compared to their counterparts. For our standard sensors, a 1 cm² device has nearly 800 cm² of exposed MWCNT surface area.

CNT based sensors have received great attention because of fast response, good sensitivity and low operating temperature [66]. Theoretical studies have confirmed the remarkable change in electronic properties of CNT due to the detection of gas molecules
Most analyte molecules are known to be either an electron-acceptor such as NO$_2$ and O$_2$ or an electron donor such as NH$_3$ and H$_2$ displaying relatively small charge transfer between weakly adsorbed molecules on the CNT wall. Multiwalled carbon nanotube (MWCNT) thin films show p-type semiconducting behavior of decreasing resistance upon exposure to NO$_2$ gas [68, 69]. CNT sensors require an external stimulus like heat or an electric pulse or high energy UV light to desorb the chemisorbed molecules from the surface. The sensor exhibits variation of the electrical resistance of CNT films in the adsorption–desorption cycles and reproducible recovery in the operating temperature range of 25–250°C [68-70].

We now know many of the fundamental properties of carbon nanotubes. One of the big questions is how to control growth so that we can grow any length we want and any chiral structure we want. Therefore, understanding the growth mechanisms in different reactors is a hot area of study. Another and somewhat separate question is how to manufacture bulk quantities of carbon nanotubes at low cost.

The commercialization of carbon nanotube technologies is currently retarded by the lack of a reliable, large-volume production capacity, the high price of the nanotubes, and little selectivity in controlling the properties of the product. Recent advances in synthesis techniques, in particular CVD methods, show promise for being scalable (ton/day), low cost (<$100/kg), and able to produce high product purity and selectivity. However, industrial-scale production will not proceed until a profitable market exists. Paradoxically, a market for nanotubes will not develop until they can be obtained in bulk quantities at prices competitive to existing materials.

4.2. Research problem

Gas detection instruments are increasingly needed for industrial health and safety, environmental monitoring, and process control. To meet this demand, considerable research into new sensors is underway, including efforts to enhance the
performance of traditional devices, such as resistive metal oxide sensors, through Nano Engineering. Metal oxide sensors have been utilized for several decades for low-cost detection of combustible and toxic gases. However, issues with sensitivity, selectivity, and stability have limited their use, often in favor of more expensive approaches. Recent advances in nanomaterials provide the opportunity to dramatically increase the response of these materials, as their performance is directly related to exposed surface volume.

In the past, many researchers have reported on using individual, network films, or bundles of CNTs for both capacitive and resistive sensors [71-76]. However, manipulating individual or bundles of CNTs into a sensor design often involves cumbersome and expensive processing steps. This factor is limiting the commercialization and expandability of nanotube based sensors in the existing market.

A thin graphite-like layer (a-C layer) is formed as a bi-product of the CVD process on the surface of nanotubes, which contributes with sp2 electronic states. This thin conducting layer plays a crucial role in determining the device baseline resistance and thus the sensitivity of these sensor devices. Many groups characterized this layer to be graphene while some report as amorphous carbon. Tailoring the thickness of this thin layer is challenging and novel etching techniques are being explored.

MWNT based sensor devices with unfunctionalized nanotubes have been reported demonstrating detection of low concentration of gases like NH₃ and NO₂ under ambient conditions [77, 78]. The sensing mechanism is due to charge transfer between the analyte gas molecules and the semiconducting nanotubes, which changes the conductivity of the nanotubes. In recent times, research has been focused on improving the sensitivities of CNT based sensors by functionalizing the nanotubes [79 – 85].
4.3. Solution to research problem

In the past, many researchers have reported on using individual, network films, or bundles of CNTs for both capacitive and resistive sensors. However, integrating individual or bundles of CNTs into a sensor design often involves cumbersome and expensive processing steps. In this context, the authors propose a simple MWCNT sensor device design which does not require manipulation of individual or bundles of tubes, or any techniques like e-beam or photolithography.

MWCNTs grown on Silicon substrates were integrated in sensor design and evaluated for their sensor response. This novel design allows obtaining higher sensitivities when compared to the conventional device configurations due to the available higher surface area of the nanotubes. The large surface area is not only due to inner surface, surface area between the cores of a MWCNT but also due to the exposed outer surface of the nanotube where the gas has high probability of being adsorbed.

The thickness of a thin amorphous carbon layer formed as a byproduct of the CVD growth process can be tailored either during the process of nanotube growth or by various post growth techniques, like plasma, electrochemical, and chemical treatments. Among them, plasma etch technique have the advantage of being non-polluting and providing a wide range of control parameters such as power, gases used and duration of etch process. As part of this research, the variation of a-C layer, and the dependence of device sensitivities on different micro wave plasma etch conditions was thoroughly investigated. Also, the change in the absorption abilities of analyte species onto the surface of nanotubes was extensively studied.

The MWCNT based sensor design proposed as part of this research provides for a large well-defined surface area and the capacity for modifying the carbon nanotube surface with various transduction materials to effectively enhance the sensitivity and broaden the scope of detectable analytes.
This can be achieved by the preparation of nanocomposites with the combination of Carbon Nanotubes, conducting polymers (CPs) and metal nanoparticles by various techniques like self-assembly, electrochemical and sol–gel process[86 –90]. Composite materials based on the coupling of conducting polymers and CNTs have been shown to possess properties of the individual components with a synergistic effect [91]. In particular, the transport properties of CNT films can be greatly enhanced by doping them with CPs. Synthesis of CNT – CP composites also provides a great room for tailoring the electronic and mechanical properties of these materials. In particular, they offer an attractive route to introduce new electronic properties based on morphological modifications or electronic interactions between the two constituents [92-96]. In general, there are two basic processes: either the polymer functionalizes the CNTs and/or the polymers are doped with CNTs. Functionalization of CNTs can be covalent or non-covalent i.e. different interactions between the nanotube surface and the CP take place depending on the synthesis technique.

The main objective of this study is to investigate various MWCNT based composite films for gas sensing applications with a special attention given to MWCNT-conducting polymer nano composites. In this chapter, we demonstrate the use of polymers like polyaniline (PANI) and poly (3,4-ethylenedioxythiophene)–polystyrene sulfonic acid (PEDOT:PSS) to enhance the gas sensing capabilities of CNT based composite sensor devices. PANI is selected because of the flexibility to tailor its electrical and other physical properties by the type of solvent used [97, 98]. Also, recent studies show that the nanocomposites of CNTs and PANI have enhanced the sensing properties of CNTs [99,100]. PEDOT:PSS, due to its many interesting properties like high conductivity and high stability in its p-doped form, is one of most successful commercially available polymers. PEDOT:PSS with H₂O as a solvent is optically transparent, well spin-coated, and a hole transport material. The increase in conductivity that PEDOT:PSS provides with the addition of solvents like DMSO, lead to various applications including electromagnetic radiation shielding and a better electrical
transport. Even though, there exists several reports on fabrication of CNT-polymer nano-composite films and solvent effects on polymer conductivity [100], our work is a unique attempt to fabricate CNT-polymer nanocomposites through a simple process, integrate them into a sensor design and demonstrate selectivity to analyte gases.

4.4. Experimental Procedures

4.4.1. Materials

PEDOT:PSS and POLYANILINE polymers were commercially available. High purity Polyaniline was purchased from Alfa Aesar while aqueous dispersion of PEDOT: PSS (Baytron P) was purchased from Bayer. The PEDOT: PSS was an aqueous dispersion of the conductive polymer, PEDOT/PSS. The weight ratio of PEDOT to PSS was 1:1.6, and the mixture was diluted with H$_2$O. Prime grade p-type (100) Silicon wafers with a resistivity of 0.005 Ohm-cm purchased from University Wafers were used as substrate materials.

4.4.2. Growth of Multi Walled Carbon Nanotubes

Fabrication of MWCNTs was started with the growth of 200nm thick silicon dioxide via thermal oxidation of silicon wafers which served as substrates for nanotube growth. MWCNT growth was then carried in a horizontal tube CVD reactor system, previously described by Andrews et al [101]. Approximately 6.5 mol% of ferrocene (Fe catalyst particle source) was dissolved in xylene (hydrocarbon source) to obtain feed solution with $\sim$0.75 at% Fe/C ratio. This liquid was then pumped at the rate of 1ml/hr into the pre heater zone of the two stage reactor using a syringe pump. The preheater maintained at 240°C volatizes the precursor liquid and swept into the reaction zone maintained at 800°C by the carrier gas. The carrier gas is a mixture of H$_2$ and Ar gas flowing at 75sccm and 675sccm respectively creating a reducing atmosphere inside the
furnace (90%Ar/10%H₂). The reaction time was selected as 20min for obtaining a dense and uniform nanotube deposition.

4.4.3. Materials characterization

Scanning electron micrographs (SEM) have been taken with field emission scanning electron microscopy (FE-SEM, S-4300 HITACHI). A Varian 7000 FT-IR research step-scan spectrometer was used to characterize the polymer –MWCNT composite. Nanosecond TRS capabilities, fast kinetic scan rates, and spectral coverage from the far-IR to the UV make this uniquely versatile spectroscopy an ideal characterization technique for polymer and polymer based composites.

4.4.4. Preparation of polymers

Baytron P (PEDOT:PSS) and organic solvents were mixed by the volume ratio of 3:1 (PEDOT/PSS: organic solvent). The solvents used were dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF) and 0.1M NaOH. The mixed solution was then rigorously stirred for 24 h at room temperature. On the other hand, solvents like 2-Propanol, Ethylene Glycol, dimethyl sulfoxide (DMSO) and N,N dimethyl formamide (DMF) were used to dissolve the Polyaniline from Alfa Aesar. PANI was dissolved in these organic solvents in the ratio of 50mg of PANI in 30ml of solvent. The mixture was thoroughly stirred for 24h at room temperature and care was taken to make sure that there was no residue left after dissolution. Table 4.2 lists the details of polymers and their doping solvents with corresponding sample names.
Table 4.2: Table listing details of polymers and their corresponding doping solvents

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>As prepared</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>DMF</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>DMSO</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>0.1M NaOH</td>
</tr>
<tr>
<td>POLY ANILINE</td>
<td>DMSO</td>
</tr>
<tr>
<td>POLY ANILINE</td>
<td>DMF</td>
</tr>
<tr>
<td>POLY ANILINE</td>
<td>2-Propanol</td>
</tr>
<tr>
<td>POLY ANILINE</td>
<td>Ethylene Glycol</td>
</tr>
</tbody>
</table>

4.4.5. Gas sensor fabrication

For gas sensing experiments, the polymer solutions (both PEDOT:PSS and PANI) were spin-coated onto MWCNT films grown on Silicon/Silicon dioxide substrates. The polymers were spin coated twice onto the nanotube films at a speed of 2000 RPM. The samples were vacuum baked at 100°C for an hour. These films were then integrated into sensing devices (figure 4.3) by depositing 0.2cm X 2cm contact electrodes (Au bus bars) via e-beam evaporation technique using an aluminum foil shadow mask.

![Figure 4.3: Schematic of resistive sensor design](image-url)
4.4.6. Plasma Etch Technique

In order to uniformly etch the a-C layer formed on the samples, a custom made microwave plasma etch apparatus was used. The samples were placed in a glass chamber evacuated to a pressure of 30 inches of Hg and a controlled flow of gas (Oxygen) was introduced inside the chamber. The etch process was performed with the processing time adjusted between 30sec and 120sec.

4.4.7. Measurement of sensing properties

All the MWCNT based sensor devices were evaluated for their sensor response by measuring the change in resistance across the two bus bars when exposed to analyte (Test Gas) and Nitrogen. A HP 3478A digital multimeter, interfaced with Lab View software, was employed to continuously monitor the change in resistance. The sensor response was evaluated by measuring the sensitivity on exposure to various gases. The sensitivity (S) is defined as,

\[
S(\%) = \frac{R_{gas} - R_{N_2}}{R_{N_2}} \times 100
\]

Where \(R_{N_2}\) is the device resistance in the presence of carrier gas N\(_2\), and \(R_{gas}\) is the resistance in the presence of test gas. S is a figure of merit for evaluating the sensor performance in that devices with higher sensitivities would yield measurable signal output for even lower concentrations of analyte gases.
4.5. Results and Discussions

4.5.1. MWCNT Characterization

The resulting MWCNT arrays after CVD growth were observed to be grown as thick films with nanotubes standing on the Silicon oxide surface as shown in figure 4.4.

Figure 4.4: (a) Cross section image of a MWCNT film grown on top of Si/SiO$_2$ substrate; (b) Top view of a MWCNT film after the a-C layer is completely removed via plasma etch

Transmission electron microscopy was used to characterize the MWCNTs synthesized on Silicon substrates as shown in figure 4.5. These observations revealed that the average outer diameter of the free-standing nanotubes was around 40nm. The distribution was very uniform with only a few tubes larger than 40nm diameter. The wall thickness of the nanotube was 5 nm on either side making the inner diameter 25 nm as shown in figure 4.5(b). From the TEM observations, the distance between two neighboring fringes was about 3.4 Å, in agreement with the inter-planar separation of graphite (3.35 Å). Also, TEM observations revealed that the tube walls were smooth with homogeneous thickness. The growth of carbon nanotubes appears to be initiated by the iron particle deposited on the silicon substrate after decomposition of the Xylene precursor with Ferrocene catalyst in it in a reducing ambient. The diameter of the
MWCNTs is also observed to be dependent on the geometry of the iron catalyst particle and hence an optimum condition for the growth was selected for synthesizing nanotubes as part of this study ensuring uniform nanotube growth.

![Figure 4.5: (a) Nanotubes after dissolving the AAO template in 50% H₃PO₄ medium; (b) Transmission electron micrograph of the multi walled carbon nanotube grown in AAO template; distance between two neighboring fringes (walls) is about 3.4 Å.](image)

The MWCNTs deposited as thin films on the Si/SiO₂ surfaces were carefully collected and dispersed in an aqueous to infer the optical properties of the Carbon Nanotubes. Absorption spectrum of a material being studied is usually obtained against a specific background, in this case the spectrum obtained from the aqueous medium used to uniformly disperse the nanotubes. Figure 4.6 shows the UV-Vis absorbance spectra of MWCNTs suspended in aqueous medium where the peak absorbance of CNT suspension was observed at 252nm which corresponds to CNT absorbance peak [102, 103]. The absorbance depends on the amount of nanoparticles in the solution. In addition, other secondary parameters such as particle size, shape, dispersion, stability,
etc. are also the keys in determining the absorption behavior. High surface area of CNTs is another reason for higher absorbance in CNT suspension.

![UV-Vis absorption on MWCNT's](image)

**Figure 4.6: UV-Vis absorbance spectra of MWCNTs suspended in aqueous medium**

### 4.5.2. Oxygen Plasma Etch

The MWCNTs fabricated on Si/SiO$_2$ substrates via chemical vapor deposition technique were integrated into sensor designs and evaluated for their gas sensing characteristics. The nanotube growth was initiated by Fe nanoparticles deposited on silicon dioxide surface which were supplied by the continuous flow of precursor into the growth chamber [104]. The nanotubes then grew perpendicular to the substrate forming a uniform MWCNT film, with the height of nanotubes depending on reaction time as shown in figure 4.7(a). Nanotubes with a length of 60 µm, obtained for a CVD growth time of 20min were used for this study.
A thin layer of amorphous carbon (a-C) is formed as a by-product of the CVD process on top of this nanotube film; this layer plays a key role in the sensor response. The a-C layer thickness can be varied between 5nm and 40nm by either tailoring the CVD growth process conditions or by post growth processing. The reaction time and temperature determine the thickness of a-C layer during the CVD growth process; while its thickness can be varied by plasma etch technique as part of post growth processing. In this paper, we report Oxygen plasma etch technique for tailoring the a-C layer thickness. Figure 4.7(b) shows the as-grown MWCNT film on a Si/SiO₂ substrate with a thin a-C layer (~10 nm) formed during the growth.

Figure 4.7: Scanning Electron Micrograph of a MWCNT film grown on Si/SiO₂ substrate; (a) Cross sectional image of the MWCNT film after 60 sec Oxygen plasma etch, the nanotubes are grown uniformly spanning a length of ~60μm and the a-C layer is completely removed; (b) Top view showing a thin layer of a-C layer providing a conduction path between the contact electrodes.
The microwave plasma etch technique reported in this study provides the following three fold advantage

i. The plasma etch technique can controllably reduce the thickness of amorphous carbon layer formed as a by-product during the CVD growth process. Change in its thickness changes the resistance of amorphous layer which in turn varies the conduction path thus playing a crucial role in determining the device sensitivity [105]

ii. The thickness of a-C layer can be tailored precisely by varying parameters like microwave power, time of etch and reduce the layer thickness to a point where the catalysts used in the fabrication of nanotubes are exposed at the surface. This results in enhancement of device performance as the metallic nano particles also play an active role in gas detection [106]

iii. Additionally, the excited species (ions) within the plasma interact with the nanotube surface breaking the C-C bonds and creating active sites for the bonding of functional groups [107]

Figure 4.8 shows the sensor response of MWCNT based thin film gas sensors to 100ppm of NH$_3$ after oxygen plasma etch. Samples were subjected to various plasma etch times and their corresponding sensor behavior was studied. The samples were initially exposed to Nitrogen gas for 10 minutes to eliminate any traces of analyte gases present in the sensing chamber. Analyte gas was then purged for 25 minutes starting from t=10 minutes. A gradual change in resistance was observed for respective analyte gases. At t=35 minutes, a combination of N$_2$ flush + UV light were used to desorb the adsorbed molecules.

As the MWCNT sensor is exposed to analyte gas, both physisorption and chemisorption take place. Weakly bonded, physisorbed molecules are easily desorbed through a N$_2$ flush whereas strongly bonded (chemisorbed or physisorbed at the defect sites) molecules are hard to desorb as their binding energy is high. Heat or ultraviolet
light is required to desorb these strongly bonded analyte gas molecule and bring the MWCNTs back to its initial conducting state [108]. This has been discussed in more detail in our earlier publication [109] and also in a later section of this document where we discuss MWNT-PEDOT:PSS composite sensor cycling response (figure 4.24).

![Figure 4.8: Response of MWCNT film to 100ppm of Ammonia (NH₃) for various oxygen plasma etch conditions](image)

Figure 4.8 show the change in resistance of MWCNT film sensors subjected to various oxygen plasma etch durations when exposed to 100ppm of NH₃. Oxygen plasma treatment introduces defects like vacancies not only on the walls of MWCNTs but also at the open ends. If a vacancy is functionalized with O₂, dissociation is observed, resulting in one C=O and C-O-C functional group [110,111]. The presence of large number of C - O functional groups after the oxygen plasma treatment results in increased adsorption of analyte molecules and thus yielding to higher sensitivities. On the other hand, MWCNT films when exposed to O₂ plasma for prolonged durations results in the formation of
carbonyl groups rather than hydroxyl groups, although OH groups have higher interaction energy with a perfect CNT wall as compared to other types of oxygen-containing groups \[111]. Thus, plasma etch technique has the following two opposing effects on the device sensitivity.

(i) A larger number of Ammonia molecules are adsorbed by CNTs during the exposure to analyte gas not only because the intervening a-C layer is thinner but also due to the additional sites created by the plasma etch process. This adsorption of additional ammonia molecules leads to increase in sensitivity.

(ii) The sheet resistance of a-C layer increases because its thickness has been reduced. This has the effect of increased isolation of individual CNTs from the electrodes so that the change in total resistance measured between the two electrodes is more decoupled from the change in the resistance of individual CNTs. This affect of a-C layer sheet resistance on device sensitivity has been observed and quantified in our earlier work on sensors based on MWCNTs embedded in the pores of alumina membranes \[105].

It follows that the device sensitivity can increase with etch time, depending upon which of the above two processes is dominant. For our device, the effects of these two mechanisms mentioned above seem to be roughly equal and opposite for etch time between 0-120 sec. However, for an etch time of 135secs, the a-C layer had become so thin that the mechanism (ii) becomes more dominant and CNTs are isolated from electrodes, thus drastically lowering the sensitivity to 0.88%. An etching time of 60secs was chosen as the best condition after rigorous testing. Testing included functionalization of nanotube films with various polymers and integrating them into sensor devices.

Figure 4.9 shows the response of a MWCNT based sensor device to 100 ppm of NO\(_2\) after subjecting to various oxygen plasma etching conditions. The increase in the resistance or positive % sensitivity when exposed to a reducing gas (NH\(_3\)) and decrease
in resistance when exposed to oxidizing gas (NO₂) implies a p-type semiconducting nature for the nanotubes [117].

![Graph showing response of MWCNT film to 100ppm of Nitrogen dioxide (NO₂) for various oxygen plasma etch conditions.](image)

**Figure 4.9**: Response of MWCNT film to 100ppm of Nitrogen dioxide (NO₂) for various oxygen plasma etch conditions

4.5.3. MWCNT/ PANI composite films

PANI, consisting of repeating units with entities at different relative weights (figure 4.10) exists in one of its three idealized states: Leucoemeraldine base (LB), Emeraldine base (EB) and Pernigraniline base (PB). LB is a reduced state with γ=1 and PB is an oxidized state with γ=0 while EB is an intermediate state with γ=0.5. PANI-CNT composites are synthesized usually in three different ways: chemical polymerization, direct mixing of CNTs with polymers and electro chemical synthesis. It was shown that, direct mixing of CNTs with polymers and chemical polymerization of aniline in the presence of CNTs result in different materials [112]. Also, the direct mixing methodology
does not drastically change the CNT properties while the chemical polymerization technique may lead to breaking of nanotubes into small fragments when the polymerization of monomers is carried out in an acidic medium.

![Figure 4.10: Schematic of PANI molecule](image)

Scanning electron microscopy images of CNT-PANI composite films are shown in figure 4.11. Higher magnification image indicates an uniform coating of polymer around the nanotube surface. A simple conformal coating of polymer around the nanotube surface in unlikely to cause a change in the sensor response of the CNT based sensor devices. On the other hand, a covalent functionalization of the polymer with a nanotube affects the vibrational modes of the nanotubes, thus explaining our results.

![Figure 4.11: Scanning Electron Micrograph of MWCNT-PANI composite film on Si/SiO₂ substrate; (a) Top view of the composite film; (b) Higher magnification image of nanotube – polymer matrix showing conformal coating of the polymer around the nanotubes](image)
TEM image of the CNTs – PANI nanocomposites as shown in figure 4.12 clearly indicates that the walls of the multiwalled carbon nanotubes are crystalline. Also, the PANI polymer was observed to homogeneously coat each nanotube in a conformal way. The PANI polymer is coated uniformly to a thickness ca. 1.5 nm on each side of the nanotube. Therefore, it is reasonable to infer that; functionalization of CNTs by PANI plays a crucial role in optimizing the signal transduction between the electrodes when integrated in this sensor design.

![TEM image of CNTs - PANI nanocomposites](image)

**Figure 4.12: Transmission electron micrograph of a MWCNT coated with PANI on both sides**

Figure 4.13 shows the FT-IR spectrum of functionalized multi walled carbon nanotubes with various PANI solutions. The primary absorption bands identified at 830.3, 1144, 1303, 1497, 1588 cm\(^{-1}\) can be attributed to the bending of C-H (out of plane) on benzene ring, bending of C-H (in-plane) on benzene ring, mode of N = Quinoid ring (Q)=N, stretching of C\(_{\text{aromatic}}\)-N and stretching of N=Q=N respectively.
Figure 4.13: FT-IR Spectra of MWCNT/PANI composite films; PANI doped with various solvents including DMF, DMSO, 2-Propanol and Ethylene Glycol was used to functionalize the CNT film

From the spectrum, it is evident that the intensity of the 1144 cm\(^{-1}\) band varies with different solvents. A higher intensity (very similar to the PANI polymer itself) was
observed for ethylene glycol solvent. On the other hand, the $1144\text{cm}^{-1}$ band was observed to be of a very low intensity and disappeared when DMF was used as a solvent. This increase in intensity is determined by the increase in the molecular dipole moment which occurs when the solvent induces positive charges on the polymer chains. Thus, the $1144\text{cm}^{-1}$ band illustrates a charge transfer mechanism between the polymer and the nanotube surface which in-turn plays a crucial role in determining the signal transduction from adjacent nanotubes to the metal electrodes when these composite materials are incorporated into sensor devices. The absence of the $1110\text{cm}^{-1}$ band indicates that there is no interaction between the nanotubes and the PANI–EB quinoid rings while the charge transfer is the dominant mechanism after functionalization. This type of interaction is usually observed in PANI-CNT composites synthesized via electrochemical reaction. The observance of all the characteristic peaks of PANI in the CNT/PANI composite films implies that the PANI is successfully attached to the multiwall nanotubes.

Figures 4.14 and 4.15 represent the typical response–recovery characteristics of the MWCNT – PANI composite film sensors to 100 ppm of NH$_3$ and NO$_2$ respectively. The sensors were first exposed to N$_2$ gas for 10 minutes, followed by 100 ppm of test gas for 25 minutes at a constant rate of 500 sccm and the change in resistance was continuously monitored and plotted with respect to time. The resistance was observed to increase when exposed to NH$_3$ gas and decrease when exposed to NO$_2$ gas suggesting a p-type behavior of the composite film.
Figure 4.14: Response of MWCNT – PANI composite films to 100ppm of Ammonia (NH₃) after 60sec Oxygen plasma etch

Figure 4.15: Response of MWCNT – PANI composite films to 100ppm of Nitrogen Dioxide (NO₂) after 60sec Oxygen plasma etch
PANI when existing as an emeraldine salt exhibits p-type semiconductor nature [113]. Hence, when ammonia is chemisorbed onto the film surface, there is a localization of polarons on the conducting PANI and thus an increase in the device resistance. After the exposure of test gas for 25 minutes, the sensor devices are exposed to pure nitrogen ambient for 10 minutes to observe their recovery response. During this period, the ions chemisorbed onto the PANI surface are desorbed, restoring the PANI molecule back to its proton state. Also, previous reports [109] suggest that the MWCNTs fabricated by xylene pyrolysis exhibited p-type semiconducting nature. The absorption of a reducing agent like NH$_3$ onto the nanotube surface would then result in a reduced hole density thereby increasing the resistance. However the persistence of resistance enhancement after the test gas is stopped may be attributed to the fact that the NH$_3$ is not only physisorbed but also chemisorbed onto the nanotube surface. The physisorbed molecules are easy to desorb and require no external agitation while the chemisorbed molecules require a high energy external excitation for desorption. As part of this investigation, a portable 100W UV light source was used as an external agitation source.

A sensitivity of 2.2% was observed for MWCNT composites sensor doped with PANI dissolved in 2-propanol when exposed to 100ppm of NH$_3$ as shown in figure 4.14. Similarly, sensitivities of 2.1%, 1.8% and 1% were observed for samples doped with PANI dissolved in DMF, Ethylene Glycol and DMSO respectively. On the other hand, the MWCNT – PANI composites exhibited enhanced sensitivities to 100ppm of NO$_2$, an oxidizing species (figure 4.15). A high sensitivity of -29.8% was observed for a MWCNT sensor doped with PANI – dissolved in DMSO solvent. While sensitivities of -28.6%, -27.6% and -25.7% were observed for samples doped with PANI dissolved in 2-propanol, DMF and Ethylene glycol respectively. MWCNT-PANI composites predominantly showed a selective response to oxidizing agent NO$_2$.

The response – recovery characteristics of a MWCNT-PANI composite sensor to 100ppm NO$_2$, when DMSO is used as a solvent is shown in figure 4.16. Sensitivities of
33.43% for the first pulse, 6.1% dynamic steady state and 35.4% cumulative were observed. The sensor was exposed to alternate cycles of NO\textsubscript{2} and N\textsubscript{2} gas to elucidate the desorption characteristics. Reason for the inability of device resistance to recover to the initial value during desorption cycle can be attributed to the fact that the analyte molecules adsorbed at defect sites on CNT walls were harder to desorb [109].

![Graph](image.png)

**Figure 4.16**: Response-recovery characteristics of MWCNT – PANI composite sensor to 100ppm of NO\textsubscript{2} after 60sec oxygen plasma etch; DMSO used as solvent

### 4.5.4. MWCNT/ PEDOT:PSS composite films

PEDOT: PSS (figure 4.17) is often used as a hole injection layer in organic photovoltaic and display devices. Because of its many attractive electrical, electrochemical and mechanical properties, there has been a lot of interest in PEDOT PSS/CNT composites in recent times [114, 115]. Lota et al. [63] reported the fabrication
of PEDOT/CNTs nanocomposite electrode that exhibits excellent electrochemical characteristics not only in acidic and alkaline media but also in organic media. Additionally, Zhang et al [117] reported fabrication of transparent, conductive, and flexible CNT films with relatively smooth surfaces through PEDOT:PSS passivation. However, CNTs are insoluble in most of the solvents due to their inert surface nature and strong Van der Waals [118]. In the following investigation, we report functionalization of CNTs by PEDOT:PSS, which plays a crucial role in determining the structural as well as electrical properties of the resulting composite films.

Applications in displays, Photo-Voltaics

![PEDOT:PSS molecule](image)

Figure 4.17: Schematic of PEDOT:PSS molecule

A distinct change in morphology of nanotube surface due to the coating of PEDOT:PSS polymer can be perceived from the SEM micrographs shown in figure 4.18. An uniform composite film was formed where PEDOT:PSS was conformally coated on all the individual nanotubes.
Figure 4.18: Scanning Electron Micrograph of MWCNT - PEDOT: PSS composite film on Si/ SiO₂ substrate; (a) Top view of the composite film showing conformal coating of the polymer around the nanotubes; (b) Higher magnification image of nanotube – polymer matrix.

The TEM image of the CNT-PEDOT:PSS in figure 4.19 also reveals the coating of PEDOT- PSS layers on the outer walls of the CNTs with a thickness of 10–12 nm, suggesting that a thick layer of PEDOT:PSS is deposited when compared to PANI shown in figure 4.10. Additionally, these images provide evidence of the uniformity of polymer coating on the outer surfaces of nanotubes which is in agreement with the SEM and the FTIR observations. From these results, we concluded that both polymers, PEDOT:PSS and PANI are successfully coated onto the outer surfaces of the MWCNTs resulting in a uniform CNT-polymer matrix.
The FT-IR spectrum of CNT/ PEDOT:PSS composite films is depicted in figure 4.20. The band at 1600cm\(^{-1}\) resembles the stretching of C = C and 1007cm\(^{-1}\) corresponds to C–H. These two bands are attributed to the aromatic rings in PSS. Bands at 1268 and 1158cm\(^{-1}\) are representative of asymmetric and symmetric vibrations of –SO\(_3\) group, respectively [119]. Additionally, the vibrations at around 1360–1574 cm\(^{-1}\) correspond to C–C and C= C stretching of quinoidal structure and ring stretching of thiophene ring (similar to benzoidal structure) [120]. 1000cm\(^{-1}\) band is assigned to the stretching modes of the C–O–C bond, and the peak at 920cm\(^{-1}\) is corresponding to the ethylenedioxy group in the molecule deformation mode [121]. Also, the C–S bond vibrations in the thiophene ring are found at 920 and 860cm\(^{-1}\). All characteristic transmission bands in various CNT/PEDOT:PSS composite films suggest that CNTs were successfully functionalized with PEDOT: PSS.
Figure 4.20: FT-IR Spectra of MWCNT/PEDOT:PSS composite films; PEDOT:PSS doped with various solvents including DMF, DMSO and 0.1M NaOH was used to functionalize the CNT film

MWCNT- PEDOT:PSS polymer composite sensors exhibited excellent sensitivities to both reducing (NH₃) and oxidizing (NO₂) species as shown in figures 4.21 and 4.22 respectively. Sensitivities as high as 28% was observed for a MWCNT sensor doped with
PEDOT:PSS when exposed to 100ppm of NH\textsubscript{3} as show in figure 4.21. The MWCNT – PEDOT:PSS composite sensors were characterized for their response – recovery characteristics where the polymer was doped with various solvents. Sensitivities of 16.6%, 5.9% and 2.5% were observed for PEDOT:PSS composite samples doped with DMSO, DMF and 0.1M NaOH respectively.

![Graph showing response of MWCNT-PEDOT:PSS composite films to 100ppm of Ammonia (NH\textsubscript{3}) after 60sec Oxygen plasma etch]

**Figure 4.21: Response of MWCNT – PEDOT:PSS composite films to 100ppm of Ammonia (NH\textsubscript{3}) after 60sec Oxygen plasma etch**

MWCNT- PEDOT:PSS composite sensors also exhibited excellent sensitivities for 100ppm NO\textsubscript{2} (figure 4.22) Sensitivities of -27.8%, -22.4% and -14.4% were observed for PEDOT:PSS composites doped with 0.1M NaOH, DMF and DMSO respectively. Similarly, -18.45% sensitivity was observed for a sample doped with just PEDOT:PSS polymer.
Figure 4.22: Response of MWCNT – PEDOT:PSS composite films to 100ppm of Nitrogen Dioxide (NO\textsubscript{2}) after 60sec Oxygen plasma etch

In figure 4.23, the sensor responses of 12.48 % for the first pulse and 3.4 % for the dynamic steady state are observed when a MWCNT- PEDOT: PSS (DMSO) composite sensor is exposed to alternate cycles of NH\textsubscript{3} (100 ppm) and N\textsubscript{2} gas for 10 minutes each. It is seen that the cumulative device resistance increases during the first three cycles, although the amplitude of the cyclic variation in device resistance (dynamic, steady state sensitivity) is practically constant, at 3.4%. Typically, the cumulative resistance continues to increase with each new exposure to ammonia cycle until a saturation state is reached at about 20 cycles; however, during this entire period, the cyclic amplitude of change in resistance remains constant at 3.4%.
Figure 4.23: Response-recovery characteristics of MWCNT – PEDOT:PSS (DMSO) composite sensor to 100ppm of Ammonia (NH₃) after 60sec Oxygen plasma etch

To study the effect of cycling, devices were subjected to a large number of cyclic exposures (10 minutes each) of ammonia and nitrogen. Results are shown in figure 4.24. It is observed that with each exposure to ammonia cycle, the cumulative resistance increases until a saturation value is reached at about 20 cycles; however the cyclic amplitude of change in resistance remains practically constant. This phenomenon can be understood in terms of two types of adsorptions of ammonia molecules by the MWCNTs,

i. Physisorption of Ammonia molecules by MWCNTs, which can respond to the cyclic changes in exposures because physisorbed molecules can be easily desorbed by the 10 minute Nitrogen+ UV exposure.

ii. Chemisorption of Ammonia molecules which are hard to desorb during the 10 minute exposure to Nitrogen + UV, resulting in a buildup on the MWCNT surface. This buildup of ammonia molecules causes an upward drift in the baseline
resistance as well as the sensitivity with each cycle, until a saturation value is attained after about 20 cycles.

Figure 4.24: Cycle life study of MWCNT – PEDOT:PSS composite sensor to 100ppm of Ammonia (NH₃) after 60sec Oxygen plasma etch

Table 4.3 summarizes the responses of various MWCNT – polymer composites for both oxidizing (NO₂) and reducing agents (NH₃) at room temperature. It can be seen that the as prepared PEDOT:PSS – MWCNT composite sensor exhibited sensitivities of 28% for NH₃ and -18.45% for NO₂. On the other hand, for the case of PEDOT:PSS doped with 0.1M NaOH solution, the sensor showed a rapid decrease in NH₃ sensitivity and a significant increase in NO₂ sensitivity. This indicates that the MWCNT-PEDOT:PSS composite sensor was made selective to NO₂ detection when 0.1M NaOH was used as a solvent. Similarly, MWCNT-PANI composite sensors showed a response of 1% for NH₃, -29.8% for NO₂ when DMSO was used as a solvent and 1.8% for NH₃ and 25.7% for NO₂ when Ethylene Glycol was used as a solvent.
Table 4.3: MWCNT- polymer composite sensor responses to NH$_3$ and NO$_2$ at room temperature; listed are the details of polymers and doping solvents used with corresponding sensitivities

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Baseline resistance</th>
<th>NH$_3$ sensitivity</th>
<th>NO$_2$ sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>As prepared</td>
<td>315.3 Ω</td>
<td>28%</td>
<td>-18.45%</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>DMF</td>
<td>331.9 Ω</td>
<td>5.9%</td>
<td>-22.40%</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>DMSO</td>
<td>199.4 Ω</td>
<td>16.6%</td>
<td>-14.40%</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>0.1M NaOH</td>
<td>1.10 kΩ</td>
<td>2.5%</td>
<td>-27.80%</td>
</tr>
<tr>
<td>POLY ANILINE</td>
<td>DMSO</td>
<td>405.8 Ω</td>
<td>1.0%</td>
<td>-29.80%</td>
</tr>
<tr>
<td>POLY ANILINE</td>
<td>DMF</td>
<td>673.4 Ω</td>
<td>2.1%</td>
<td>27.60%</td>
</tr>
<tr>
<td>POLY ANILINE</td>
<td>2-Propanol</td>
<td>630.7 Ω</td>
<td>2.2%</td>
<td>-28.60%</td>
</tr>
<tr>
<td>POLY ANILINE</td>
<td>Ethylene Glycol</td>
<td>533.3 Ω</td>
<td>1.8%</td>
<td>-25.70%</td>
</tr>
</tbody>
</table>

4.6. Conclusions

High purity thick multiwalled carbon nanotube films are grown on Si- SiO$_2$ substrates via CVD technique. A thin layer of amorphous carbon (a-C) formed as a byproduct of the CVD growth process plays a crucial role in determining the devise sensitivities. A simple, inexpensive microwave oxygen plasma etch technique was used to tailor the thickness of a-C layer. We have demonstrated a method to fabricate, integrate and evaluate MWCNT –polymer composites for gas sensing applications. Different solvents including DMF, DMSO, 2-Propanol and Ethylene Glycol were used to dope the PANI and PEDOT:PSS polymers to change their electrical and chemical properties. The fabrication technique allows a great control over the device sensitivities and makes the composite films gas specific. This marks as a prominent step towards the commercialization of CNT based sensor technologies. The composite films were characterized by SEM, TEM and FTIR techniques corroborating the existence of polymer
as thin coatings on the walls of nanotubes. The MWCNT based composite films exhibited high sensitivities to low concentrations of both oxidizing and reducing species and their behavior to these species indicated a p-type semiconducting nature of the composite film.

The MWCNT- PANI composite sensor synthesized using this technique was observed to show superior sensitivities and excellent reversibility to 100ppm of NO₂ gas. On the other hand, PEDOT:PSS uniformly coated on the MWCNTs played a crucial role in functionalizing the nanotubes and making them gas specific. MWCNT composite sensor doped with just the PEDOT:PSS polymer recorded a sensitivity of 28.1% to 100ppm of NH₃ while the device with PEDOT:PSS doped with 0.1M NaOH recorded 27.8% sensitivity to 100ppm of NO₂. The PEDOT:PSS functionalization of MWCNTs was shown to result in enhanced sensitivities and gas selectivity.
5.1. Background

A gradual decrease in the availability and a drastic increase in the consumption of fossil fuels required the usage of sustainable and renewable resources. As a result, an increased production of renewable energy from sun and wind is being observed. Also, the development of electric vehicles or hybrid electric vehicles with low CO₂ emissions is also of great interest. Because the continuous unavailability of alternate resources including both sun and wind, there is an absolute need for the development of efficient and effective energy storage systems.

Batteries and electrochemical capacitors (ECCs) are the major forms of electrical energy storage systems. However, we need to improve their performance substantially to meet the higher requirements of future systems, ranging from portable electronics to hybrid electric vehicles and large industrial equipment, by developing new materials and advancing our understanding of the electrochemical interfaces at the nanoscale. Figure 5.1 shows the plot of power against energy density, also called a Ragone plot, for the most important energy storage systems. If a supercapacitor is used in an electric vehicle, the specific power shows how fast one can go, and the specific energy shows how far one can go on a single charge. Times shown are the time constants of the devices, obtained by dividing the energy density by the power.
Figure 5.1: Specific power against specific energy, also called a Ragone plot, for various electrical energy storage devices

5.1.1. Lithium based Batteries

In recent times, rapid technological developments have hugely increased the demand for lightweight, compact and efficient batteries for portable electronic applications [122]. Most of the popular electronic devices including laptop computers, camcorders, and cellular phones require small, efficient and highly reliable batteries. Also, diffusion of electric and hybrid cars in the commercial market produced a niche for developing advanced, high-energy-density batteries [123]. The development of high-energy-density batteries requires the use of high-capacity electrode materials that can
also offer high cell voltages $V_c$. A $V_c$ of a cell is primarily determined by the work functions of the negative (anode) and positive (cathode) electrodes. Typically a high $V_c$ is obtained in a cell configuration where, an anode and a cathode have lower and higher work functions respectively $\phi_a$ and $\phi_c$. Considering only the electron transfer between the two electrodes, a schematic energy diagram at open circuit is illustrated in Figure 5.2 and the open-circuit voltage $V_{oc}$ of the cell is given as

$$V_{oc} = (\phi_c - \phi_a)/e$$

where $e$ is the electronic charge[124]

![Schematic energy band diagram of a cell (at open circuit)](image)

**Figure 5.2: Schematic of energy band diagram of a cell (at open circuit)**

To prevent unwanted reduction or oxidation of the electrolyte and ensure thermodynamic stability, the Fermi energy levels $E_F$ of the cathodes and anodes need to lie within the band gap $E_g$ of the electrolyte, as shown in figure 5.2.

Lithium metals due to high specific capacity and standard oxidation potential (smaller work function $\phi_a$) are ideal as anode materials in the development of high-energy-density batteries. Lithium technology batteries consisting of a lithium anode and
a lithium insertion compound \( \text{Li}_x\text{M}_y\text{X}_z \) \((\text{M} = \text{transition metal and X = nonmetal})\), with a larger work function \( \varphi_c \) for \( \text{M}^{n+} \) as the cathode. This configuration results in high cell voltages according to equation (1). However, the open circuit voltage \( V_{oc} \) of a battery cell is not only determined by the electron transfer, but also depends on the energy effects associated with the \( \text{Li}^+ \) transfer. Therefore, \( V_{oc} \) of a lithium cell can be more appropriately described by the difference of the lithium chemical potential between the cathode \( (\mu_{\text{Li(c)}}) \) and anode \( (\mu_{\text{Li(a)}}) \) [125].

\[
V_{oc} = \left( \mu_{\text{Li(c)}} - \mu_{\text{Li(a)}} \right) / ne
\]

Where, \( n \) and \( e \) are the number of electrons transferred and electronic charge respectively.

Lithium batteries offer several advantages, such as higher voltages, higher energy density, and longer shelf life compared to other systems. Also, the use of non-aqueous electrolytes in lithium battery technologies permits their operation over a broad range of temperatures. Figure 5.3 compares the gravimetric and volumetric energy densities of various rechargeable systems [126] prevailing in the current market. It can be deduced that lithium battery technologies are lighter in weight and smaller in dimension when compared to their contemporaries.
5.1.2. Lithium Insertion Compounds

The several advantages of lithium based batteries instigated the research and development of lithium insertion compounds in the 1970s, resulting in the identification of several insertion compounds as cathodes [127-130]. Figure 5.4 compares the electrochemical potential ranges of some lithium insertion compounds with respect to the lithium metal.
A lithium insertion compound usually consists of a host matrix into/from which the guest species Li\(^+\) can be reversibly inserted/extracted during the discharge/charge process. For the successful functioning of a lithium insertion compound as an electrode host in the lithium cells, it has to have the following properties [131]:

i. The transition metal ion in the insertion compound cathode \(\text{Li}_x\text{M}_y\text{X}_z\) should have a larger work function \(\phi_c\) for \(M^{n+}\) to maximize the cell voltage (equation 1). On the other hand, if the insertion compound \(\text{Li}_x\text{M}_y\text{X}_z\) is to be used as an anode, then the \(M^{n+}\) ion should have a smaller work function \(\phi_a\) to maximize cell voltage. The change in cell voltage, \(\Delta(\phi_c - \phi_a)/e\) or more appropriately \(\Delta(\mu_{\text{Li}(c)} - \mu_{\text{Li}(a)})/ne\), during the lithium insertion/extraction (discharge/charge) process should be small so that the operating cell voltage does not vary significantly.

ii. The insertion compound \(\text{Li}_x\text{M}_y\text{X}_z\) should allow an insertion/extraction of a large amount of lithium \(x\) to maximize the cell capacity. A high cell capacity together with a high cell voltage can maximize the energy density.
iii. The lithium insertion/extraction process should be reversible with no or minimal changes in the host structure over the entire range \( x \) of lithium insertion/extraction.

iv. The insertion compound should support good electronic (\( \sigma_e \)) and Li+ ion (\( \sigma_{Li} \)) conductivities to minimize cell polarizations. The high conductivities are essential to support a large current density and hence to provide a high power density.

v. The insertion compound should be chemically stable over the entire voltage range without undergoing any reaction with the electrolyte.

vi. From a commercial point of view, the insertion compound should be inexpensive, environmentally friendly, and lightweight to minimize the battery weight.

5.1.3. Electro-Chemical Capacitors

Table 5.1 compares some of the fundamental properties of secondary (rechargeable) batteries and electrochemical capacitors (ECCs) and illustrates the major differences between them. The fundamental difference between a battery and an electrochemical capacitor is that the battery stores energy in the bulk of chemical reactants capable of generating charge, whereas an ECC stores energy directly as surface charge. Battery discharge rate and therefore power performance is then limited by the reaction kinetics as well as the mass transport. Because Li-ion batteries are limited by the slow power delivery or uptake, faster and higher-power energy storage systems are needed in a number of applications. ECCs are power devices that can be fully charged or discharged in seconds; as a consequence, their energy density (about 5 Wh kg\(^{-1}\)) is lower than in batteries, but a much higher power delivery or uptake (10 kW kg\(^{-1}\)) can be achieved for shorter times (a few seconds). They have had an important role in complementing or replacing batteries in the energy storage field, such as for uninterruptible power supplies (back-up supplies used to protect against power disruption) and load-leveling. A more recent example is the use of electrochemical
double layer capacitors (EDLCs) in emergency doors (16 per plane) on an Airbus A380, thus proving that in terms of performance, safety and reliability ECs are definitely ready for large-scale implementation.

Electrochemical capacitors currently fill the gap between batteries and conventional solid state and electrolytic capacitors (figure 5.1). They store hundreds or thousands of times more charge (tens to hundreds of farads per gram) than the latter, because of a much larger surface area (1,000–2,000 m² g⁻¹) available for charge storage in EDLC.

It is usually difficult to precisely measure the state-of-charge (SOC) of a battery due to its constant operating voltage which is limited by the thermodynamics of the reactants used. On the other hand, for a capacitor, its operating voltage changes linearly with time during constant current operation so that the SOC can be precisely determined. Also, the highly reversible electrostatic charge storage mechanism in ECCs does not lead to any volume change like observed in batteries with electrochemical transformations of active masses. This volume change limits the cyclability of batteries generally to several hundred cycles whereas ECCs has demonstrated from hundreds of thousands to many millions of full charge/discharge cycles.

Hence, ECCs are considered as potential energy storage devices due to their exhibit high power density, excellent pulse charge–discharge properties, excellent reversibility and long cycle life [132]. Table 5.1 summerizes the comparison between batteries and electrochemical capacitors. There has been a lot of research in the last decade on these devices because of their diversified applications in electronic devices, such as power electronics, as well as in hybrid electric vehicles and space flight technology [133, 134]. Figure 5.5 shows a schematic representation and optical images of commercially available electrochemical capacitors.
Based on the charge-storage mechanism, electrochemical capacitors are mainly classified into electric double layer (EDL) capacitor and pseudocapacitor. An EDL capacitor stores energy in the electrode/electrolyte interface of its double layer. Therefore, electrode materials of high specific surface area increase the capacitance of the applied EDL capacitor. Many report the usage of high-surface-area carbon as an electrode material for EDL [135–138].

Table 5.1: Comparison of properties of secondary batteries and electrochemical capacitors

<table>
<thead>
<tr>
<th>Property</th>
<th>Battery</th>
<th>Electrochemical Capacitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage mechanism</td>
<td>Chemical</td>
<td>Physical</td>
</tr>
<tr>
<td>Power limitation</td>
<td>Electrochemical reaction kinetics, active materials conductivity, mass transport</td>
<td>Electrolyte conductivity in separator and electrode pores</td>
</tr>
<tr>
<td>Energy limitation</td>
<td>Electrode mass (bulk)</td>
<td>Electrode surface area</td>
</tr>
<tr>
<td>Output voltage</td>
<td>Approximate constant value</td>
<td>Sloping value - state of charge known precisely</td>
</tr>
<tr>
<td>Charge rate</td>
<td>Reaction kinetics, mass transport</td>
<td>Very high, same as discharge rate</td>
</tr>
<tr>
<td>Cycle life limitations</td>
<td>Mechanical stability, chemical reversibility</td>
<td>Side reactions</td>
</tr>
<tr>
<td>Life limitation</td>
<td>Thermodynamic stability</td>
<td>Side reactions</td>
</tr>
</tbody>
</table>

However, a major problem of this carbon material is the incomplete accessed surface area: not all the area is electrochemically accessible by electrolyte [139]. On the other hand, pseudocapacitor not only stores energy in its electrochemical double layer but also stores energy within the host materials through electrochemical faradic reactions. In addition to high-surface area, diffusion of proton in host materials also influences the capacitance of pseudocapacitor, especially at high-rate charge/discharge. Consequently, nanostructured materials are promising for pseudocapacitor application due to their reduced diffusion paths and increased specific surface area. The majority of pseudocapacitors fall into two main subclasses: (i) metal oxides in aqueous electrolyte
and (ii) conducting polymers that work both in aqueous and nonaqueous electrolytes [142, 143].

Figure 5.5: Electrochemical capacitors. (a) Schematic of a commercial spirally wound double layer capacitor; (b) Assembled device weighing 500 g and rated for 2,600 F. (Photo courtesy of Batscap, Groupe Bolloré, France); (c) A small button cell, which is just 1.6 mm in height and stores 5 F (Photo courtesy of Y-Carbon, US.). Both devices operate at 2.7 V.

5.2. Research problem

Initially, transition metal sulfides were considered as ideal cathode hosts however, it was difficult to achieve higher cell voltages with sulfides [144]. Stabilization of higher oxidation states in lithium insertion compounds LiₓMᵧX₂ is important for the enhancement of φₓ and thus the cell voltages. Also, the location of the O-2p energy much below the S-3p energy makes the higher valent states accessible in transition metal oxides. Hence, the transition metal oxide hosts yield the highest operating cell voltages around 4V. Moreover, the Fermi energy levels Eₖ of both cathode and anode are kept within the bandgap of non aqueous electrolytes used in lithium cells. Due to
their higher cell voltage (~4V), the layered LiMO₂ (M = Co and Ni) and the spinel Li[Mn₂]O₄ are considered as the prominent cathode materials among the available lithium insertion compounds [145, 146]. The higher voltage is due to the larger work function \( \phi_c \) associated with the highly oxidized Co\(^{3+}/4^+\), Ni\(^{3+}/4^+\), and Mn\(^{3+}/4^+\) couples in an oxide.

However, there are a few issues with the LiMO₂ (M= Co and Ni) and Li[Mn₂]O₄ cathodes. Most of the electrolytes decompose due to oxidation above ~4.3 V. Also, degradation of cathode limits the use of Li\(_{1-x}\)MO₂ (M = Co and Ni) to \( x < 0.5 \) which lowers the utilizable capacity to <150 mAh/g [147]. Metals like cobalt and nickel are expensive and toxic. Also, the reversibility of lithium insertion/extraction in LiMO₂ is strongly controlled by the ordering of Li\(^+\) and M\(^{3+}\) ions in the lattice [148, 149] which in turn determines the performance of the cell. LiCoO₂ can be readily obtained as an ordered material but is expensive. On the other hand, LiNiO₂ is difficult to obtain as an ordered, stoichiometric material because nickel tends to form Ni\(^{2+}\) [150,151]. The cost and environmental concerns of cobalt and nickel make the spinel Li[Mn₂]O₄ more attractive because manganese is inexpensive and environmentally friendly. But the Jahn-Teller distortion associated with the Mn\(^{3+}\) ions causes capacity fading upon cycling, and also limits the utilizable capacity to <120 mAh/g, corresponding to a lithium extraction/insertion of 0.4 Li per Mn. Also, the carbon anode exhibits an initial loss in capacity probably due to side processes involving decomposition of the electrolyte.

Metal oxide materials have been the main focus of research for developing supercapacitors utilizing pseudocapacitance. Ruthenium oxide is the most widely investigated metal oxide for pseudocapacitors because of its fairly high specific capacitance [152, 153]. However, the high cost of RuO₂ has prompted the search for other transition metal oxides such as MnO₂, NiOₓ, MoO₃, Co₃O₄, Fe₃O₄ and V₂O₅ [154–157].
5.3. Solution to problem

There is enormous interest to develop environmentally compatible and less expensive metal oxide electrodes. Also, there are several research groups developing novel materials for anode applications. The performance of the cathode materials can be enhanced by innovative synthesis and fabrication procedures. This research focus on the low-temperature synthesis procedures employed in recent years both to develop new oxide electrodes and to overcome the difficulties of the known electrode hosts. As part of this research work, we fabricated high density and high aspect ratio Ni and Mo nanowires via electro-deposition technique. Electro-deposition is an inexpensive and safe technique which also provides kinetic accessibility to metastable phases and unusual valence states in the metals. Additionally, the structure, stoichiometry / composition and chemical properties of the materials can be easily controlled by tuning the applied potentials and electrolyte ingredients.

To enhance the performance of electrochemical capacitors, there is a great interest in developing new electrode materials that exhibit higher specific energy while retaining its intrinsic high specific power. The major classes of materials used as electrodes for ECCs include various forms of carbon, transition metal oxides, and conductive polymers. Because the key factors determining the performance of ECCs are the specific surface area (SSA) of electrode materials and the properties of electrolytes, understanding and modifying the surface properties are crucial in achieving high power and energy density.

Development of nanostructured electrode materials for electrical energy storage devices aids in obtaining higher energy capabilities in these devices. Recent reviews have shown that designing nanostructured materials of pseudocapacitive nature such as oxides, nitrides and carbides [158, 159] is a novel methodology to achieve high specific capacitance. The nanostructured electrode design offers higher specific capacitances and energy densities when compared to their bulk counter parts due to the advantages like
• very large specific surface area
• enhanced reaction kinetics
• shorter diffusion paths
• reduced contact resistance between the active material and current collector and
• Large ionic contact area

Hence, it is possible to maximize the contribution of the active material to capacitance. Additionally, nanostructured electrodes provide improved power delivery and increased cycling stability.

Additionally, increase in volume of the active material due to several lithium intercalation and de-intercalation process when implemented as electrodes in Li based batteries can be buffered with the nanostructured electrode design. This reduces the dominant mechanical stresses observed in bulk electrode film materials which results in cracking and thus cell failure. Figure 5.6 is a schematic of a nano-architecture electrode where nanorods/nanowires are grown on a metallic current collector.

Figure 5.6: A schematic representation of the expected advantages of nanostructured electrodes with 1D nanowires grown assembled on the metallic current collector [160]
As part of this research, a novel nano-architected electrode configuration was designed by fabricating highly ordered arrays of one-dimensional (1D) nanostructures (nanowires and nanotubes) on a highly conducting metallic current collector. Accordingly, each 1D nanostructure of active material possesses a better point contact to current collector and provides expedited ionic diffusion pathways throughout the electrode that could maximize the electrical energy storage ability.

This research work mainly focuses employing 1D Molybdenum and Nickel oxide nanowire based electrodes for Li based batteries and electrochemical capacitors. Molybdenum oxides (MoO$_2$ and MoO$_3$) have significant uses in energy related devices such as fuel cells and lithium batteries [161–163]. Reports are available on the application of poly(3,4-ethylenedioxythiophene)–MoO$_3$ nanocomposites, MoO$_3$ nanowires, MoO$_3$ supported on activated carbon or glassy carbon materials as electrodes for supercapacitors [164–168].

Molybdenum oxides (MoO$_3$ and MoO$_2$) are very attractive electrode materials among numerous transition metal oxides due to their rich, unusual chemistry produced by the multiple valence states, and their high activity for Li ion batteries and ECCs. Orthorhombic phase MoO$_3$ is provided with an intrinsic capacious crystalline structure that readily inserts/extracts (reversibility) ions of surface redox couples [169] and hence is expected to exhibit an ultrahigh pseudocapacitance [170]. Despite all that, the aligned array of nanowire electrode structure has a higher surface-to-volume ratio and can be potentially used to fabricate large area, highly sensitive, and more stable devices. However, the research on the fabrication and application of aligned NiO and MoO$_3$ nanowire based electrodes for Li based batteries are comparatively rare. Due to their low cost and good electronic conductivity, these materials can also constitute a good electrode for Electro chemical capacitors.
5.4. Experimental procedures

5.4.1. AAO membranes and current collector

Commercially available free standing Whatman Anodisc 13 membranes were used as the starting materials. The pores were 150-200nm in diameter, 60microns in length and a porosity of ~30%. Thin film (20-50 nm) of gold was sputtered on one of the free standing AAO membranes using a DC-sputter technique to enable conduction for further processing. Thick film of Nickel was then electrodeposited onto the gold film serving as a current collector.

5.4.2. Electrodeposition

Template assisted electrodeposition is a simple and inexpensive technique to fabricate nanostructures when compared to chemical vapor deposition and other methodologies. Electrodeposition process usually involves an electrolyte along with a working and counter electrode. On application of an electric signal, the ionized particles are created in the electrolyte and the ions are attracted to their respective electrodes. Thus, for electrodeposition of metals, ionized metal atoms in the electrolyte are reduced at the cathode; which is the working electrode. However, for this study a three-electrode electrodeposition cell was adopted as shown in figure 5.7 where AAO membrane with pre-deposited nickel serves as the working electrode, platinum metal is the counter electrode and Saturated calomel is the reference electrode.
5.4.3. Nickel plating bath

Plating of a high purity nickel collector is very crucial to determine the contact resistance of the electrode assembly. Watts bath was used as the electrolyte for electrochemical deposition of metallic Nickel. In this bath, Nickel chloride and Nickel Sulphate supply the ion sources for nickel within the bath. The bath composition is as follows

Table 5.2: Table showing chemical composition of Watts bath

<table>
<thead>
<tr>
<th>Watts Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 g/L NiCl₃</td>
</tr>
<tr>
<td>300 g/L Ni(SO₄)₃</td>
</tr>
<tr>
<td>30 g/L Boric Acid</td>
</tr>
<tr>
<td>3 g/L Saccharin</td>
</tr>
</tbody>
</table>
5.4.4. Molybdenum plating bath

Various plating bath chemistries were investigated in this work for electrodeposition of metallic molybdenum. Initial plating baths were adapted from [172] the molybdenum plating bath chemistries in the literature. All chemicals were reagent grade and were purchased from Alfa easeer and Fisher Scientific Company. The source of Molybdenum for these baths was Soldium Molybdate (Na₂MoO₄) and Molybdenum trioxide (MoO₃). The chemical compositions of each plate bath used for this study are shown in table 5.3. All baths were adopted from Bath 1 and Bath 4 and different only in the concentration of the constituents.

Table 5.3: Table showing the chemical compositions of electroplating baths formulated for a volume of 200ml

<table>
<thead>
<tr>
<th>Bath 1</th>
<th>Bath 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.839 gm Na₂MoO₄</td>
<td>4.17834 gm Na₂MoO₄</td>
</tr>
<tr>
<td>10.6994 gm NH₄Cl</td>
<td>10.6982 gm NH₄Cl</td>
</tr>
<tr>
<td>Add NH₄OH; ph ~ 9</td>
<td>Add NH₄OH; ph ~ 8.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath 3</th>
<th>Bath 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.839 gm Na₂MoO₄</td>
<td>4 gm MoO₃</td>
</tr>
<tr>
<td>10.6994 gm NH₄Cl</td>
<td>2 gm Na₄P₂O₇</td>
</tr>
<tr>
<td>7.5 gm Na₄P₂O₇</td>
<td>Add NaHCO₃ (7 gm); ph ~ 8</td>
</tr>
<tr>
<td>Add NH₄OH; ph ~ 8</td>
<td>Add NH₄OH; ph ~ 8.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath 6</th>
<th>Bath 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 gm MoO₃</td>
<td>10 gm MoO₃</td>
</tr>
<tr>
<td>6 gm Na₄P₂O₇</td>
<td>5 gm Na₄P₂O₇</td>
</tr>
<tr>
<td>Add NaHCO₃ (7 gm); ph ~ 8</td>
<td>0.5 gm SLS</td>
</tr>
<tr>
<td>Add NaHCO₃ (8.5 gm); ph ~ 7.5</td>
<td>Add NaHCO₃ (8.5 gm); ph ~ 7.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 gm MoO₃</td>
</tr>
<tr>
<td>5 gm Na₄P₂O₇</td>
</tr>
<tr>
<td>0.5 gm SLS</td>
</tr>
<tr>
<td>1.5 gm Saccharin</td>
</tr>
<tr>
<td>Add NaHCO₃ (8.5 gm); pH ~ 7.5</td>
</tr>
</tbody>
</table>
For Baths 1, 2 and 3, Na₂MoO₄ was the source of Molybdenum and Ammonium hydroxide (NH₄OH) was used for adjusting the pH of plating bath. On the other hand, for baths 4, 6, 7 and 8, MoO₃ was the source of Molybdenum and sodium hydroxide was used to adjust the plating bath pH. Sodium Pyro Phosphate (Na₄P₂O₇) was used as a complexing agent in all plating baths except bath 1 and 2. Saccharin, has been used as an organic additive in plating bath 8 to reduce the internal stress of deposits and to refine the grain structure [168].

5.4.5. Electrodeposition of Nickel

Electrodeposition of metals was carried out in an electro-chemical cell as shown in figure 5.7. A Gamry PCI-400 Potentiostat/Galvanostat was used to perform the electrochemical deposition and analysis. For deposition of Ni current collector, the AAO membrane coated with thin Au film was immersed into Watts bath and used as a working electrode connected via a copper tape. A cathodic deposition at 1.3 volts was performed for 20 minutes to deposit Ni current collector such that it is thick enough to completely seal the pores on one side of template as shown in figure 5.8. Deposition was carried at 60°C under constant stirring of the bath.

Figure 5.8: Schematic showing AAO membrane and thick nickel current collector electro-deposited covering pores on one side
Nickel current collector deposited AAO membranes were then glued onto a copper tape using silver epoxy and the remaining copper surface was covered with nail polish. This is a very crucial step for electrochemical deposition as the metals might deposit wherever it is conductive thus decreasing the thickness of the desired metallic film.

The prepared sample was then immersed in the watts bath and Ni nanowires were cathodically deposited at 1.2V for 12 minutes. Prior to the deposition, the sample was immersed in the bath for 15 minutes to make sure the pores and wetted by the electrolyte. Care was taken that bath was maintained at 60°C during the deposition under constant stirring.

5.4.6. Electrodeposition of Molybdenum

There are two different modes of electrodeposition, potentiostatic and galvanostatic modes, which are carried out by controlling the deposition potential and the current respectively. Both of these two modes have been investigated for the deposition of molybdenum nanowires. In Potentiostatic deposition, the abrupt increase in the deposition potential results in a settlement of current after sometime. On the other hand, galvanostatic deposition is carried at a constant current and the potential takes a few seconds to reach equilibrium.

Several Galvanostatic and Potentiostatic deposition conditions were explored for the different bath compositions mentioned in table 4.3. However, the experimental set-up is similar as described in the previous section where a nickel current collector coated AAO membrane glued to a copper tape was immersed in the respective bath acting as a working electrode while platinum sheet and saturated calomel serves as counter and reference electrode respectively. All plating baths were maintained at 60°C and continuously stirred during the electrodeposition process.
5.4.7. Electrode preparation

Upon completion of the electro deposition process, the samples were rinsed in DI water and dried in nitrogen flow. Samples were then immersed in 1M NaOH solution for an hour at room temperature to remove the alumina matrix. Samples were again rinsed thoroughly in DI water and vacuum dried. Samples were then treated with Acetone for 30 minutes to remove any unwanted nail polish and silver epoxy resulting in a highly dense metal nanowire arrays vertically standing and firmly attached to nickel current collector as shown in figure 5.9.

Molybdenum and Nickel nanowire samples were annealed at 500°C and 400°C for two hours in order to obtain their respective oxide forms.

![Figure 5.9: Schematic showing vertically aligned metal nanowire arrays attached to nickel current collector after removal of AAO matrix](image)

5.4.8 Lithiation of metal nanowires

As part of this study, as-prepared metal nanowire, metal oxide nanowire and pre Lithiated metal oxide nanowire based electrodes were tested as electrodes in
different configurations. Lithiation of as-prepared metallic nanowires was achieved by anodic oxidation of the same in an aqueous LiOH solution. The free standing vertically aligned metal nanowires on Nickel current collector were immersed in a 4M LiOH bath and anodically oxidized at a current of 10mA for 30 minutes. The Lithiated and oxidized metal nanowires were subsequently annealed at 500°C for 5 hours to achieve crystalline Lithiated metal oxide structures.

5.4.9. Swagelok cell assembly

An electrochemical study of electrode materials synthesized requires working in inert atmosphere inside a glove box or using a sealed cell. The most commonly used cells in regular laboratory lithium battery studies are the coin-type cell and the Swagelok® cell. As part of this research, all electro chemical studies that required the usage of lithium were performed in a two electrode Swagelok cell. A picture of the Swagelok® cell (assembled) along with a cross-section scheme is presented in figure 5.10. It consists of a Duplex Swagelok® tube fitting (a hollow Teflon cylinder, which has a male NPT thread at each side), two metallic plungers made of steel, and two perforated nuts.
Figure 5.10: Swagelok cell (a) Cross sectional schema showing various components of the Swagelok cell assembly; (b) Optical image showing the assembled Swagelok cell used for this study

The electrode is placed on one plunger onto which two separators (Celgard-coated high porosity Polypropylene membranes) are placed and soaked with an electrolyte solution. The separators play a crucial role in the cell assembly as they not only insulate the working and counter electrodes preventing from shorting but also enable ion transport through the electrolyte between the electrodes. A standard electrolyte Ethylene Carbonate (EC)/diethyl carbonate (DEC) / lithium hexafluorophosphate (LiPF₆) was used. The counter-electrode material, metallic lithium mounted onto a titanium mesh, is placed over the separator. The titanium mesh not only provides mechanical support for the thin metallic Lithium but also enables better
current collection. A cross sectional schematic of the electrode assembly is shown in figure 5.11.

![Figure 5.11: A cross sectional schematic showing the electrode assembly including the working electrode, separators and the counter electrode (metallic lithium)](image)

A stainless steel spring ensures an optimal electrical contact. The plungers are held in place by the nuts, while tightness is provided by plastic joints. The Swagelok cell once optimally tightened is used for further electro chemical characterization.
5.5. Results and discussions

5.5.1. Nickel nanowires

As mentioned in the earlier sections, Nickel current collector was electrodeposited on one side of the AAO membrane at a potential of -1.2V in a 3-electrode configuration with saturated calomel as the reference electrode. The plating bath was continuously stirred and maintained at 60°C during the plating process. As the plating was performed potentiostatically, the variation of current with respect to time was noted. A typical current - time plot for the Ni current collector electroplating is shown in figure 5.12.

![Figure 5.12: A typical current – time graph plotted during the electro deposition of Nickel as a current collector](image)

The electroplating condition of nickel current collector was optimized such that (i) there is enough thickness of nickel deposition on one side of the template completely covering the pores and not getting deposited inside the pores as shown in figure 5.13 (a)
and, (ii) top surface of the AAO membrane is clean without any deposition as shown in figure 5.13 (b).

![AAO membrane after the deposition of Nickel current collector](image)

Figure 5.13: AAO membrane after the deposition of Nickel current collector; (a) Cross sectional micrograph showing the bottom with no metal inside the pores; (b) Micrograph showing a top view of the AAO membrane with open pores and no deposition

Nickel nanowire deposition was performed as mentioned in section 5.3.5. A cathodic deposition at 1.2V with respect to the saturated calomel electrode for a period of ten minutes was performed. The duration of electro-deposition depends on the desired length of nanowires. For better nucleation of metal ions inside the pores, initially, a high cathodic potential of 1.5V was applied for a few seconds (2-3 seconds) and then the electroplating was performed at 1.2V. A typical current-time plot during the deposition of Nickel nanowires is shown in figure 5.14.
Dependence of the nanowire length on the deposition time was thoroughly studied and the micrographs are shown in figure 5.15. The typical deposition rate of 1-1.3 µm/min was observed for a Potentiostatic deposition of Ni nanowires in watts bath at -1.2V for a pore diameter of 150nm.

Figure 5.16 shows micrographs of free standing, vertically aligned Nickel nanowires attached to nickel current collector after the removal of AAO membrane. It can be observed that the deposition was dense and uniform throughout the electrode surface. Nanowires were 20-25µm long with a diameter of 150nm.
Figure 5.15: Cross-section images of Nickel nanowires electrodeposited in AAO membranes using watts bath; (a) Potentiostatic deposition at -1.2V for 20min; (b) Potentiostatic deposition at -1.2V for 30min; (c) Potentiostatic deposition at -1.2V for 36min; (d)(e) and (f) Nickel nanowires at different magnification
Figure 5.16: Micrographs of free standing Nickel nanowires on Nickel current collector after the etching after AAO membrane; (a) Top view showing Ni nanowires; (b) Higher magnification image showing bundles of nanowires; (c),(d),(e)and(f) Cross-sectional micrographs showing high density, high aspect ratio, vertically aligned Nickel nanowires attached to nickel current collector.
Figure 5.17 represents the XRD patterns of the as deposited Nickel nanowires. The diffraction peaks located at $44.5^\circ$, $51.8^\circ$ and $76.4^\circ$ correspond to Ni (111), (200) and (220) face respectively (JCPDS 4-850).

![XRD diffraction pattern of as deposited Nickel nanowires](image)

**Figure 5.17: XRD diffraction pattern of as deposited Nickel nanowires**

After annealing the as-deposited Nickel nanowires in oxygen at $400^\circ\text{C}$, diffraction peaks at $2\theta = 37.3^\circ$, $43.3^\circ$ and $62.9^\circ$ were observed as shown in figure 5.18. These peaks correspond to cubic structure NiO (101), (012) and (110) face, respectively (JCPDS 44-1159). There were no impurities and hydroxide peaks observed in the XRD profiles. Previous reports indicate that electrochemically deposited nickel oxide and nickel oxy-hydroxide contain structural water in the solid oxide phase [171]. The water content in the metal-oxide structure induces challenges in Lithium ion battery applications because of the instability of Lithium with water during the charge/discharge processes [172]. Heat treatment at higher temperatures circumvents this problem. Therefore in this work, the annealing temperature was selected as $400^\circ\text{C}$ to convert the as-grown Nickel nanowires into NiO nanowires.
Figure 5.18: XRD diffraction pattern of as Nickel oxide (NiO) nanowires; as-deposited nickel nanowires annealed in O\textsubscript{2} at 400\textdegree C for 2 hours

Figure 5.19 shows cross sectional micrographs of Lithiated Nickel oxide nanowires. Nanowires were still vertically aligned after the anodic Lithiation suggesting a good contact between the current collector and the metal nanowires. It was observed that the surface morphology of lithiated nickel nanowires was significantly different to the as-prepared nanowires. From the higher magnification image, it can be observed that the texture (surface) was uniform thorough out the length of the nanowires.
Figure 5.19: Micrographs showing cross-sectional view of free standing, vertically aligned nickel nanowires anodically lithiated at a current of 10mA and annealed in oxygen at 400°C; (a) Lower magnification image showing free standing nanowires; (b) Higher magnification image indicating a change in surface morphology of nanowires after lithiation

5.5.2. Molybdenum nanowires

In the past there have been very few reports on the template assisted growth of molybdenum nanowires via electrochemistry. As part of this research, several bath chemistries were formulated as mentioned in section 5.4.4 and tested for various deposition conditions. Various deposition conditions including Potentiostatic, Galvanostatic, Pulse- Galvanostatic and Pulse –Potentiostatic techniques were performed to obtain high purity Mo nanowires. Some of the key process conditions and their respective bath chemistries are discussed in this section.

Initial depositions were performed in plating bath 1 which was adopted from [173] where Sodium Molybdate was the primary salt. Figure 5.20 shows a current –time plot observed during the electrodeposition of Molybdenum nanowires in plating bath 1 at 60°C for 30minutes at a cathodic potential of 1.0V. It was observed that for this condition, the deposition was very grainy and had mostly deposited on the top surface and a very little inside the pores as shown in figure 5.21.
Figure 5.20: Typical current-time characteristics for a -1.0V Potentiostatic electrodeposition of molybdenum nanowires inside the pores of AAO membrane in plating bath 1

![Graph showing current-time characteristics](image)

Figure 5.21: Micrographs showing molybdenum electrodeposited potentiostatically at -1.0V in plating bath 1; (a) top view showing deposition on the top surface blocking the pores and; (b) very less deposition inside the pores also the deposition looks amorphous in nature

![Micrographs of molybdenum electrodeposition](image)

In order to improve the deposition characteristics, plating bath 2 was formulated which had an addition of Sodium Chloride to plating bath 1. Depositions were
performed at -1.0V to -1.2V over durations of 20min to 60min. With these conditions, the quality of metal deposition was improved but edge effects were dominant. Dense metal deposition was observed along the edges of the templates with nanowires spanning the entire length of the pore while deposition length was limited to only a few microns at the centre of the template. Various methodologies were investigated to overcome the problem of edge effects including pulse deposition technique. Edge effects were still prevalent even with DC pulse deposition. A characteristic spacing was observed between a particle that is expected to be depending on the T\textsubscript{ON} and T\textsubscript{OFF} timings of the pulsing cycles as shown in figure 5.22.

![Image](image.png)

**Figure 5.22:** Cross section image showing molybdenum deposition in the pores after DC pulse deposition. Discontinuous nanoparticles were deposited; Edge effects were still existent

Plating bath 6 was formulated and Molybdcic acid (MoO\textsubscript{3}) was used as the primary salt supplying molybdenum ions. Sodium pyrophosphate, a complexing agent was added to the plating baths in order to enhance the ionization of salt in electrolyte and improve the quality of deposited metal. Plating bath 6 showed improved depositions and the edge effects were minimized to an extent where they were negligible. Figure 5.23 shows micrographs of Molybdenum nanowires deposited inside the AAO membrane using plating bath 6.
Figure 5.23: Micrographs showing cross-sectional view of potentiostatically deposited molybdenum nanowires inside the AAO membrane at -1.2V for 60 minutes; (a) Lower magnification image showing deposited molybdenum; (b) Higher magnification image indicating a tubular growth of molybdenum and abnormal morphology.

Figure 5.23 (a and b) shows a dense deposition of molybdenum nanowires but the porous matrix was missing. The reason for this can be attributed to the duration of electro deposition (60 min). The plating bath is acidic in nature and longer the deposition time is the more is the hydrogen evolution and hence higher is the pH of the bath. Alumina (Al₂O₃) matrix is highly soluble in acidic medium and therefore is believed to be completely dissolved by the end of electrodeposition. Attempts were made to decrease the deposition time but still there was a significant dissolution of the AAO matrix. Also, smaller durations of electroplating resulted in a very minimum or zero deposition of the metal indicating a need for improvement in the bath chemistry.

Plating bath -7 was formulated to improve the morphology of deposited metal nanowires. Sodium Lauryl Sulphate (SLS), an organic additive was included in the plating bath. SLS is a wetting agent used commonly in electrochemical processes that reduces the surface tension of the solution thereby facilitating the hydrogen extraction from cathode deposit. Electrodeposition experiments were performed using bath 7 but no improvement was seen in the quality/morphology of the metal deposit.
Saccharin was included in plating bath -8 in addition to SLS. Saccharin is a strong leveling agent for the surface and a grain refiner. Saccharin molecules are adsorbed in a reversible way on active sites of the electrode surface, thereby increasing the number of nucleation sites and decreasing the mean free path for lateral diffusion of adatoms. This brings about an increase in frequency of 1-D nucleation that produces smooth surfaces by reducing residual stress and improving film quality. To obtain precise control over the growth of nanostructures, depositions were performed in Galvanostatic mode using plating bath -8. Figure 5.24 shows scanning electron micrographs of electrodeposited molybdenum inside the pores of AAO membrane. As mentioned in the previous section, all depositions were performed at a temperature of 60°C and the samples were allowed to soak in the bath at the same temperature for at least 20 minutes prior to deposition to for improving the wetting properties.

Addition of saccharin to the plating bath greatly helped in improving the quality of deposition and the morphology of metal surface. As shown in figure 5.24(a,b) deposited at -10mA for 60min resulted in a uniform and dense nanowire matrix. However, the dissolution of AAO matrix was still dominant. The reason could be attributed to the prolonged deposition. However, deposition times were gradually decreased in the following experiments and the dissolution of alumina was slowly reducing. For smaller durations of electrodeposition, a nucleation step was performed where, the sample was exposed to higher currents (-15mA) for a little duration of time prior to the actual deposition. This nucleation step not only enhanced the deposition characteristics but also reduced the time of deposition resulting in the survival of alumina matrix.
Figure 5.24: Micrographs showing cross-sectional view of galvanostatically deposited molybdenum nanowires inside the AAO membrane using plating bath-8; (a), (b) 10mA for 30 min; (c),(d) Dual step : 15mA for 10min, 6mA for 15min; (e)(f) Dual step: 15mA for 5min, 8mA for 20min
Improved molybdenum metal depositions were observed with plating bath-8 in comparison to the previous bath chemistries. Hence, plating bath-8 has been standardized and used for molybdenum nanowire depositions for further evaluations in this study. Figure 5.25 shows micrographs of vertically aligned free standing molybdenum nanowires electrodeposited galvanostatically using plating bath 8. AAO matrix was removed by hydroxide etch as mentioned in the previous sections. It was observed that the metal deposition was very uniform along the electrode surface with improved surface morphology.

Figure 5.25: Micrographs showing free standing molybdenum nanowires deposited galvanostatically using plating bath-8; (a), (b) Dual step: 15mA for 10min, 10mA for 5min; (c)(d) Dual step: 15mA for 2min, 8mA for 10min
Figure 5.26 shows X-ray diffraction patterns of as deposited Molybdenum metal nanowires. Diffraction peaks at $2\theta = 40.5^\circ$ and $74^\circ$ were observed. These peaks correspond to Body Centered Cubic structure Mo (110) and (211) face, respectively. Therefore, it can be deduced that the atomic planes of the BCC structured metallic Molybdenum have a lattice constant $(a) = 0.3147$ Å.

The XRD patterns of MoO$_3$ nanowires formed by annealing the as-prepared Mo nanowires in Oxygen at 500°C for 2 hours are shown in figure 4.24. The XRD diagrams exhibit predominantly the (110), (040), (021) and (060) lines at $2\theta = 23.3^\circ$, $25.6^\circ$, $27.3^\circ$ and $38.9^\circ$ respectively. These diffraction lines represent for an oriented structure of the layered $\alpha$-MoO$_3$ phase. An additional spectral line (022) at $48.2^\circ$, which is a representative of the $\beta$-MoO$_3$ phase, was also observed in the XRD spectrum. MoO$_3$ exists in two polymorphic phases (a,b). The $\beta$-MoO$_3$ phase with a monoclinic lattice related to the three-dimensional ReO$_3$ structure differs from $\alpha$-MoO$_3$ phase. It is evident that the annealing the metallic molybdenum nanowires at a high temperature (500°C) favors the growth of $\alpha$-MoO$_3$ single-phase (Figure 5.27). This structure consists of
double layers of linked distorted MoO$_6$ octahedra parallel to (010) planes. In each double layer MoO$_6$ octahedra form edge sharing zig-zag rows along [001] direction and corner sharing rows along [100] direction. Successive layers are held together by weak interlayer forces with easy cleavage along (010) planes. The ReO$_3$-type structure ($\beta$-phase) does not contain the van der Waals gap of $\alpha$-MoO$_3$.

![XRD diffraction pattern](image)

**Figure 5.27**: XRD diffraction pattern of as Molybdenum Oxide (MoO$_3$) nanowires; As-deposited Molybdenum nanowires were annealed in O$_2$ at 500°C for 2 hours

5.5.3. *Cyclic Voltammetry*

Cyclic Voltammetry (CV) is a crucial characterization that illustrates the mechanism of the electrochemical reactions in a cell setup. It is helpful in determining the potentials at which intercalation/deintercalation processes and other reactions occur. As part of this study, CV was used to examine the electrochemical behavior of both Nickel and Molybdenum oxide nanowire based electrodes when assembled as Lithium based battery as well as super capacitor applications. All the cell assemblies discussed in this work for electro chemical capacitors were tested in a half cell
configuration. A half cell configuration is a setup where the fabricated electrode is tested as a working electrode against a standard platinum or graphite as the counter electrode in a standard electrolyte.

Voltammetry techniques consist of applying a potential sweep to an electrode and recording the current flowing through the working electrode as a function of the applied potential. In the present case, the metal oxide nanowire electrode was swept between its open circuit potential and 0.1 V vs. Li at various sweep rates.

In order to describe the potential profiles obtained by this method, let’s consider that species A is present in the solution and that potential $E_r$ is the potential at which an electrochemical reaction consumes A and produces B. Initially, no current is passed since potential $E$ is not close enough to $E_r$ to induce electron transfer. When $E$ approaches $E_r$, the reaction $A^{\pm} e^{-} \rightarrow B$ begins and current starts to pass. As a result, the concentration of A decreases within the region next to the electrode (the Nernst diffusion layer), creating a concentration gradient. The current flowing is proportional to the value of this gradient. When the concentration of A approaches zero near the electrode, the concentration gradient tends to decrease due to diffusion, and so does the current. As a result, the potential profile shows a maximum, as illustrated in figure 5.28.

![Figure 5.28: Potential-current profile for a typical cyclic voltammetry experiment](image)
Especially for electrochemical capacitor devices, cyclic-voltammetry gives a useful overall basis for the characterization of the performance of the system in terms of: (i) the reversibility of the charge and discharge processes; (ii) the distinction between any distinguishable stages in the charging and/or discharging processes; (iii) the accumulated charge as a function of potential through the integration of the voltammograms; (iv) the range of potentials between which the electrodes can be operated for charge acceptance and disposal, and (v) the dynamical behavior of the electrode for charge acceptance and disposal derived from the dependence of the current-response function to increasing sweep rate, s.

Figure 5.29 shows the CV characteristics of NiO nanowire based electrodes tested at a scan rate of 0.1 mVs\(^{-1}\) in the voltage range 0.01V – 3.5V vs. metallic lithium. As mentioned in the earlier sections, the as prepared Ni nanowires were heat treated at 400\(^\circ\)C in oxygen ambient to convert them into NiO. Reduction peaks were observed to become broad with every cycle and is composed of a main peak at around 0.5 V and a low-density shoulder peak near 1.3 V. In the oxidation scan, two broad peaks are well resolved at about 1.4 and 1.8 V. The two pairs of redox peaks indicate that there are two sets of faradaic reaction involved. The well-known mechanisms for these reactions are as follows \cite{174, 175}:

\[
\begin{align*}
\text{NiO} + 2\text{Li}^{+} + 2e^{-} & \rightarrow \text{Ni}^{0} + \text{Li}_{2}O + \frac{\text{polymeric layer formation}}{\text{electrolyte reduction}} \\
\text{Ni}^{0} + \text{Li}_{2}O & \rightarrow \text{NiO} + 2\text{Li}^{+} + 2e^{-}
\end{align*}
\]
A decrease in the individual peak intensity with cycling was observed for both electrodes. Also shifting of oxidation peaks to higher potentials and reduction peaks to lower potentials was also observed. The decrease in the peak intensity density results from the irreversible capacity losses due to the incomplete redox reaction. Formation of a SEI (Solid Electrolyte Interphase) layer may also result in capacity loss with cycling. The increase in the shifting of oxidation and reduction potential peaks with cycling indicates degradation of the electrodes. However, the shape of the CV curves in the following cycles remained similar to those in the second cycle, suggesting reversible reduction and oxidation of the Ni nanowire based electrode materials.

Figure 5.30 shows profiles of CV curves obtained when pre-Lithiated NiO nanowires were tested between a potential range of 0.1V – 3.5V at a scan rate of
0.1mVs\(^{-1}\). An obvious difference was observed between the first scan cycle, especially the cathodic scan and the subsequent cycles (inset in figure 5.30).

![Cyclic Voltammograms of Lithiated Nickel oxide nanowire electrode vs metallic Lithium in LiPF\(_6\) at a scan rate of 0.1 mVs\(^{-1}\)](image)

**Figure 5.30: Cyclic Voltammograms of Lithiated Nickel oxide nanowire electrode vs metallic Lithium in LiPF\(_6\) at a scan rate of 0.1 mVs\(^{-1}\)**

During the first cathodic cycle, a reduction peak was located at around 0.4V which corresponds to the decomposition of NiO into Ni. Due to the fine particle sizes (nanowires), the reduction peak shifts to 1.0V in the 2\(^{nd}\) cathodic cycle [176]. The oxidation peaks, resulting from the re-oxidation of nanometer sized Ni nanowires to NiO were also shifted after the 1\(^{st}\) cycle and remained at the same position for the subsequent cycles. However, a slight shift of the reduction peak towards less positive potentials and a decrease in the peak currents (peak intensities) after 2\(^{nd}\) cycle were observed. This can be attributed to the structural or textural modifications or because of the formation of an SEI layer. Figure 5.31 shows the SEM images of NiO nanowires after
a complete CV testing. Clearly, the morphologies of NiO films have changed drastically when compared to the as prepared Lithiated NiO nanowires shown in figure 5.19. This change in the texture suggests that the lithium storage process in NiO nanowires is unlike the process in Lithiated compounds like graphite because the morphology of the graphite materials after Li intercalation does not change. However a significant volume change due to expansion at the time of Li intercalation and contraction during de-intercalation will be observed in the graphite based materials. These changes in volume cause mechanical stress resulting in cracking or permanent failure of the electrodes. On the other hand, nanowire based electrode structure have a very minimum change in volume and also has the ability to buffer these stresses due to their free standing aligned nature.

![SEM images of pre-lithiated NiO nanowires after CV testing](image1)

**Figure 5.31**: SEM images of pre-lithiated NiO nanowires after CV testing; (a) Cross-sectional view of freestanding NiO nanowires with SEI layer; (b) Higher magnification image showing the change in morphology of nanowires after several Lithium intercalation and de-intercalation processes

Figure 5.32 shows the cyclic voltammograms of NiO nanowire electrode measured at different scan rates of 2mVs$^{-1}$, 15mVs$^{-1}$, 20mVs$^{-1}$ and 50mVs$^{-1}$. The CV curves do not have the characteristic shape (nearly rectangular) of a pure double-layer capacitor [177] but show a similar behavior of a pseudocapacitor [178].
An electrochemical redox peak was observed when the CV was performed between 0.01V to 0.3V (versus Saturated calamol). This is because of the quasi-reversible redox process occurring during the potential sweep of porous NiO electrode. The anodic peak (positive current) is due to the oxidation of NiO to NiOOH and the cathodic peak (negative current density) is for the reverse process, which together are the signatures of pseudocapacitance behavior of porous NiO [179, 180].

\[
\text{NiO} + \text{OH}^- \xrightleftharpoons{\text{charge}} \text{NiOOH} + e^- \xrightleftharpoons{\text{discharge}}
\]

The anodic peak current densities are 1.0mA (scan rate 2mVs\(^{-1}\)), 5.6mA (scan rate 15mVs\(^{-1}\)), 6.3mA (scan rate 20mVs\(^{-1}\)) and 12mA (scan rate 50mVs\(^{-1}\)). There are small changes in the shape of the CV curves observed with scan rate. A small positive shift of the oxidation peak potential and a negative shift of the reduction peak potential have been observed with increased scan rate. The positive sweeps of CV curves are not completely symmetric to their corresponding negative sweeps, which indicates some irreversibility in the system [180, 187]. However, ideal reversible behavior of super capacitor systems cannot be achieved practically due to the prevailing polarization effects in the faradaic processes [182].

Nanowire based electrode design is better when compared to some porous electrode structures as, the Ohmic resistance due to electrolyte diffusion into the pores of the electrode results in certain kinetic irreversibility of the ions involved in the redox reaction in the latter. However, lower \(\Delta E_p\) values for lower scan rates and higher \(\Delta E_p\) for higher scan rates was observed as shown in figure 5.32.

\[
\Delta E_p = E_a - E_c; \text{ where } E_a = \text{Anodic peak potential and } E_c = \text{Cathodic peak potential}
\]
This behavior is indicative of a better reversibility at lower scan rates than at higher scan rates. A linear (quasi-linear) relationship between the anodic peak current and the scan rate was observed which suggests the occurrence of surface redox reactions and hence higher power capacities. This also corroborates the pseudo capacitance behavior of NiO electrode [183, 184].

Specific capacitance can be calculated using the current density, scan rate, and weight of the active NiO material as follows

\[
C_s = \frac{1}{\nu \cdot w \cdot \Delta V} \int_{V_i}^{V_f} i \, dV
\]

Where,
- \( C_s \) is the specific capacitance of NiO electrode in Fg\(^{-1}\);
- \( w \) is the mass of the active material (NiO) in gms;
- \( \nu \) is the scan rate (Vs\(^{-1}\))
- \( i \) is the cathodic/Anodic current in the potential range of \( V_i \) to \( V_f \)

and

\( \Delta V \) is the applied potential window in volts

Figure 5.32: Cyclic Voltammograms of NiO nanowire electrode vs platinum in 1M KOH solution at various scan rates; (a) 2 mVs\(^{-1}\); (b) 15 mVs\(^{-1}\); (c) 20 mVs\(^{-1}\); (d) 50 mVs\(^{-1}\)
The cyclic voltammograms of the Molybdenum oxide (MoO$_3$) nanowire based electrode in the first four cycles are shown in figure 5.33. The voltage was swept between 3.5V and 0.1V at a rate of 0.1mVs$^{-1}$. The first cycle presents an irreversible cathodic discharge which may relate to the reduction of solution species to form a passivating surface film on the electrode (see the small peak at about 0.4V).

![Figure 5.33: Cyclic Voltammograms of Molybdenum oxide (MoO$_3$) nanowire electrode vs metallic Lithium in LiPF$_6$ at a scan rate of 0.1 mVs$^{-1}$](image)

On the other hand, CV plot of first scan was observed to be shifted with respect to the subsequent cycles. This change in the peak intensities, especially the reduction peaks may be attributed to the formation of an initial non reversible SEI layer. However, after the first cycle, all the subsequent cycles are overlapping with each other indicating a stable electrochemical process. This in-turn indicates that MoO$_3$ nanowire based
electrodes are ideal for Li based battery applications with a minimum or zero degradation of the electrode with cycling.

Cyclic voltammograms of pre Lithiated MoO$_3$ nanowires are shown in figure 5.34. A small reactive current and a large reduction peak can be found at 0.4V in the first cathodic scan when the cell was tested from 3.5V to 0.1V at a rate of 0.1mvs$^{-1}$. This large peak may correspond to the reduction of Molybdenum oxide to metallic Mo, accompanying the formation of Li$_2$O. In addition to the large peak, the first cathodic scan also has several small reduction peaks in the voltage range of 2.5 – 1.3V which disappear in the subsequent cycles. These peaks correspond to a multi-step electrochemical lithium insertion reaction, indicating that lithium intercalations were possibly occurring at distinct energetic reaction sites within the MoO$_3$ electrode. On the second and subsequent cycles, these peaks nearly disappeared. Moreover, the oxidation peaks were broadened from second cycle onwards which may be caused due to the extraction/insertion of lithium from/in the MoO3 electrodes during the charge-discharge processes modifying the nanowire structure.
An oxidation peak at 2.25V was observed only in the first and second cycles and gradually disappeared in the subsequent cycles. This peak may correspond to an incomplete activation of electrode material during these cycles and also the formation of SEI layer. Additionally, it should be noted that the reduction current was always higher than the oxidation current. The reason for this behavior can be attributed to the fact that Li+ insertion was only partially reversible due to the inherent structure transformations during the intercalation and de-intercalation processes. Figure 5.35 (c) and (d) shows SEM images of MoO₃ nanowires after a complete CV testing. Nanowires were Lithiated and heat treated in oxygen prior to the cell assembly. The morphologies of nanowires have changed drastically when compared to the as prepared MoO₃ nanowires shown in figure 5.35 (a) and (b). This change in the texture suggests that the
lithium storage process in MoO3 nanowires is unlike the process in Lithiated graphite based materials.

![Figure 5.35: SEM images of MoO3 nanowires showing a drastic change in morphology of nanowires after several Lithium intercalation and de-intercalation processes; (a) MoO3 nanowires; (b) Pre-lithiated MoO3 nanowires.](image)

Figure 5.36 shows the cyclic voltammogram of the nickel oxide nanowires in 1M KOH at various scan rates of 5mVs\(^{-1}\), 25 mVs\(^{-1}\), 50 mVs\(^{-1}\) and 100 mVs\(^{-1}\) respectively. Redox peaks were obtained when the electrode was scanned from -0.25V to 0.3V in 1M KOH solution with Saturated Calomel as the reference electrode. The redox peaks and their corresponding currents obtained at various scan rates are summarized in table 5.4. Increase in ΔEp with increasing scan rate indicates that the electrodes exhibit reversibility at lower scan rates with compared to higher scan rates.
Table 5.4: Table listing the redox peaks and their corresponding currents when MoO$_3$ electrodes were evaluated for their capacitance in 1M KOH solution.

<table>
<thead>
<tr>
<th>Scan rate</th>
<th>Oxidation peak</th>
<th>Reduction peak</th>
<th>$\Delta E_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potential</td>
<td>Current</td>
<td>Potential</td>
</tr>
<tr>
<td>5 mVs$^{-1}$</td>
<td>0.135 V</td>
<td>1.41 mA</td>
<td>0.068 V</td>
</tr>
<tr>
<td>25 mVs$^{-1}$</td>
<td>0.140 V</td>
<td>4.46 mA</td>
<td>0.060 V</td>
</tr>
<tr>
<td>50 mVs$^{-1}$</td>
<td>0.147 V</td>
<td>7.90 mA</td>
<td>0.055 V</td>
</tr>
<tr>
<td>100 mVs$^{-1}$</td>
<td>0.155 V</td>
<td>13.5 mA</td>
<td>0.043 V</td>
</tr>
</tbody>
</table>

In addition to the redox peaks, CV result also shows that as the film is cycled between 0V and -0.1V vs Saturated Calomel, a purely capacitive current was obtained as shown in figure 5.36(a). This capacitance is a result of the electrical double-layer capacitance of the film rather than from the redox (faradaic) reaction.

Figure 5.36: Cyclic Voltammograms of MoO$_3$ nanowire electrode vs platinum in 1M KOH solution at various scan rates; (a) 5mVs$^{-1}$; (b) 25 mVs$^{-1}$; (c) 50 mVs$^{-1}$; (d) 100 mVs$^{-1}$
In general, an ideal electrical double-layer capacitor of smooth electrode surface has a current response in CVs shapes like rectangular mirror image. Apart from instrumental response problem, electrical double-layer capacitance is independent of the scan rate and the applied potential. In this case, enhanced peak currents with increase in scan rates suggest a Pseudoo –capacitive behavior for the MoO₃ based electrodes. However, through redox reactions a much higher specific capacitance can be stored in a redox capacitor when compared to a double-layer capacitor.

5.6. Conclusions

This research was concentrated developing novel metal oxide nanostructured electrode design for Lithium based batteries and electrochemical capacitors. Electrochemical deposition, an inexpensive and simple technique was adopted to fabricate Ni and Mo nanostructures via template assisted process. Additionally, Electrodeposition technique also provides kinetic accessibility to metastable phases and unusual valence states in the metals. Highly dense and uniform porous AAO matrix served as the starting material to fabricate arrays of aligned metal (both Ni and Mo) nanowires. Watts bath was used for plating Nickel while, several bath chemistries were formulated for depositing molybdenum metal as plating of molybdenum is difficult and not common. A chemical bath was thus successfully standardized after various experimentation and characterization.

Samples were then heat treated in oxygen ambient to convert them into respective oxide forms. All samples were thoroughly characterized for their physical and material properties via SEM and XRD respectively. These nanostructured materials were then assembled and tested in a Swagelok cell configuration for evaluating them as electrodes for Li based batteries. Lithium metal was used as counter electrode and LiPF₆ served as the electrolyte. These electrodes exhibited excellent electrochemical activity when characterized via Cyclic voltammetry. Both metal oxide nanowires and pre
lithiated metal oxide nanowires showed great cyclability and energy storage properties however, formation of an SEI layer was a concern.

Also, both the metal (Ni and Mo) oxide nanowire based electrodes were tested as electrodes for electrochemical capacitors via cyclic voltammetry. The samples were tested in a flooded bath configuration where SCE was the reference electrode and a platinum foil served as the counter electrode. Both the electrode structures exhibited excellent pseudo capacitive behavior especially MoO₃ electrodes. Electrodes were thoroughly tested under various scan rates and it was observed that they exhibited superior cyclability at lower scan rates.
CHAPTER 6: CONCLUSIONS

Multi walled carbon nanotubes and metal nanowire arrays fabricated via Chemical Vapor and Electrochemical deposition techniques respectively were successfully integrated into gas sensing and energy storage devices. This research was focused on the fabrication of inexpensive MWCNT based sensor devices that detect very low concentrations of hazardous gases at room temperature. Additionally, inexpensive and highly efficient electrodes based on nanostructured metal oxides were fabricated and tested for lithium based batteries and electrochemical capacitor applications.

Sensor design based on MWCNTs grown inside the pores of AAO membranes was evaluated for both oxidizing and reducing gases. The sensitivity was calculated by the change in resistance of device when exposed to alternate cycles of carrier and analyte gases. These sensors were responsive to both oxidizing and reducing species at room temperature and a detailed study was conducted on the dependence of sensitivity on the thickness of amorphous carbon layer on both top and bottom. Changes in the device resistance to different test gases interpreted in terms of a model where the MWCNTs were thought to behave as p-type semiconductors. Charge transfer between the nanotubes and the analyte is an important mechanism in changing the resistance of the sensor when exposed to NH$_3$.

An equivalent circuit model was developed to understand the operation, and propose design changes for increased sensitivity. The device is understood in terms of the splitting of current between the top a-C layer and an alternate path which includes the MWCNT’s. Additionally, the model enables a current mapping which illustrates the importance of having active MWCNT’s in the circuit. This mathematical model developed clearly elucidates the mechanism of resistance change in MWCNTs in MWCNT/AAO resistive sensor devices. The model enables improvements in sensitivity of MWNT based devices and makes their performance on par with the more expensive competitors like SWNT gas-sensing devices.
MWCNT-polymer composite films were fabricated and tested as gas sensors for both oxidizing and reducing gases. A simple, inexpensive microwave oxygen plasma etch technique was used to tailor the thickness of a-C layer and the dependence of the sensitivity of the thickness of a-C layer was thoroughly investigated. Different solvents including DMF, DMSO, 2-Propanol and Ethylene Glycol were used to dope the PANI and PEDOT:PSS polymers to change their electrical and chemical properties. The fabrication technique allows a great control over the device sensitivities and makes the composite films gas specific. This marks as a prominent step towards the commercialization of CNT based sensor technologies. The composite films were characterized by SEM, TEM and FTIR techniques corroborating the existence of polymer as thin coatings on the walls of nanotubes.

Metal (Ni and Mo) nanowires were fabricated via template assisted electrochemical deposition and tested as electrodes for lithium based batteries and super capacitor applications. These nanowire based electrodes were assembled in a Swagelok cell with metallic Lithium as a counter electrode and LiPF$_6$ as an active electrolyte. The electrodes were then tested for various electro-chemical characteristics including cyclic voltammetry and galvanostatic cycling. A superior electrochemical performance of metal oxide (Ni and Mo) nanowires was observed in comparison to the previously reported nano-particle based electrodes. The reason for this behavior can be attributed to its very high surface area and shorter diffusion lengths of the nanowire structures.
REFERENCES


125
43. Wei, Chen; Dai, Liming; Roy, Ajit and Tolle, Tia Benson 2006 J. Am. Chem. Soc. 128, 1412
53. Wei, Chen; Dai, Liming; Roy, Ajit and Tolle, Tia Benson 2006 J. Am. Chem. Soc. 128, 1412
74. J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han, M. Meyyappan, 2003 Nano Lett. 3 929
78. J. Li, Y. J. Lu, Q. Ye, M. Cinke, J. Han, M. Meyyappan, Nano Lett. 2003, 3, 929.
104. Illayathambi K, Rodney A, PinarMengǜc M and Qian D 2008 *Chemical Engineering Science* 64 1503
106. R. Ionescu et al 2006 *Sensors and Actuators B* 113 36
139. D. Qu, J. Power Sources 109, 403 (2002)
Vita

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