Development of SnO₂/PEO nanofiber gas sensor for THC detection

by

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B.Sc. in Aerospace and Mechanical Engineering, Amirkabir University of Technology, 2015

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE COLLEGE OF GRADUATE STUDIES

(Mechanical Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Okanagan)

April 2018

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Abstract

This thesis presents the development of a metal oxide semiconductor (MOS) sensor for detection of volatile organic compounds (VOCs) which is of great importance in many applications involving either control of hazardous chemicals or noninvasive diagnosis. There are numerous methods for detection of VOCs where their efficacy is assessed by their sensitivity, selectivity, recovery time and portabily. Commercial MOS sensors are embedded in a housing, blocking the gas diffusion path and also limiting their application in the handheld VOC detectors. In this research, the sensor is fabricated based on tin dioxide (SnO_2) / Poly Ethylene Oxide (PEO) using electrospinning. The sensitivity of the proposed sensor is further improved by calcination and gold doping. The gold doping of the composite nanofibers is achieved using sputtering, and the calcination is performed using a high temperature oven. The performance of the sensor with different doping thicknesses and different calcination temperatures is investigated to identify the optimum fabrication parameters resulting in high sensitivity. The results show that the sensing properties of the sensing layer, including response and recovery time, are significantly affected by the doping and calcination procedure. The optimum calcination temperature and duration are found to be 350°C and 4 hours, respectively. Also, the optimum thickness of the gold dopant is found to be 10 nm. The sensor with the optimum fabrication process is then embedded in a microchannel coated with several metallic and polymeric layers. The role of the channel is to enhance the selectivity of the sensor against different VOCs or mixtures. The performance of the sensor is compared against a commercial sensor. The comparison is performed for methanol and a mixture of methanol and Tetrahydrocannabinol (THC) which is the psychoactive element in cannabis. Segregation of the responses obtained for methanol and the mixture of methanol and THC is presented in a 3D feature space. It is shown that the proposed sensor outperforms the commercial sensor when it is embedded inside the channel. The proposed sensor integrated with the microchannel has a potential to be used as a breath analyzer for detection of THC in the breath.

Lay Summary

Devices that analyze breath for detection of different gases use sensors. Commercially available sensors need many adjustments in order to be successfully placed in breathalyzer devices, and this research aimed to fabricate a sensor which can be adjusted in the design stage for any high precision gas detector. This means that time, money, and resources are not wasted. This research explains the fabrication process of a general purposes gas sensor in detail, including the setup that was developed to place the sensing layer. This sensor was developed in such a way that makes it particularly adept at detecting marijuana biomarkers (THC molecules) in the breath. Finally, a mathematical model is used in order to detect and differentiate between gases, such as THC and other chemicals that the sensor is exposed to.

Preface

The presented research in this thesis is the original work of the author. Portions of this research have been accepted in a technical conference; furthermore, portions will be submitted for possible publication in technical journals related to sensors and actuators.

A version of chapter one will be published as a review paper in the journal of sensors and actuators. Pouria Mehrabi, Mina Hoorfar et al. (2018) "Advances in the fabrication of metal oxide semiconductor gas sensors for medical and environmental applications: a review paper", Sensors and actuators Journal. I wrote most of the manuscript and Dr. Hoorfar edited the entire article.

Chapter 2 and 3 are based on work conducted in Advanced Thermo-Fluidic Laboratory (ATFL) in the School of Engineering by Dr. Mina Hoorfar and Pouria Mehrabi. I was responsible for fabrication of sensors using verity of methods and performing the standard tests and writing the manuscript. Also a version of chapter 2 and 3 has been submitted to the Canadian Society of Mechanical Engineering (CSME) conference. Pouria Mehrabi, Mina Hoorfar et al. (2018) "Fabrication of SnO2 composite nanofiber-based gas sensor using electrospinning method", CSME Congress.

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List of Symbols

MOS	Metal oxide semiconductor
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
VOC	Volatile organic compound
PEO	Poly ethylene oxide
IDE	Interdigitated electrode
THC	Tetrahydrocannabinol
T1DM	Type 1 diabetes mellitus
PVP	Poly vinyl pyrrolidone
SnO ₂	Tin dioxide
WO ₃	Tungsten trioxide
AMT	Ammonium metatungstate hydrate
Pt	Platinum
Cr	Chromium
Au	Gold
ppm	Part per million
CVD	Chemical vapor deposition
PANI	Polyaniline
DI	Deionized

Acknowledgements

To start with, I would like to acknowledge my thanks and gratitude to my supervisor Dr. Mina Hoorfar for her great leadership and assistance during my Master studies. Her enthusiasm and dedication have always been highly motivating and inspirational, and have pushed me to become a better student and researcher.

Additionally, I would also like to thank my committee members Dr. Najjaran and Dr. Johnson for their support, advice, and guidance during the last year of my studies. I am very thankful to all of my colleagues in the Advanced Thermo-Fluidic Laboratory in the School of Engineering at UBC's Okanagan Campus, especially Justin Hui, for assisting me in the conduction of my experiments and sharing part of their lives with me.

Finally, I would like to express my heartfelt thanks to my family who have always loved and supported me throughout my life and arduous years of education.

Dedication

This work is dedicated to

My beloved family for their endless support and encouragement

Chapter 1: Introduction

1.1 Background

Olfaction systems play an important role. Gas detection sensors (referred sometimes to as artificial olfaction systems) are widely used in different applications including but not limited to: medical applications (such as disease diagnosis based on patient's biomarkers) [1], oil and gas pipe line leakage detection [2], aircraft manufacturing [3], [4], safety, environmental and air quality control [5], [6]. Depending on the application, gas sensors with different sensitivity (the change in the response as a function of the concentration) and selectivity (the ability to detect a group or single gas) are required. Some applications even require real-time measurement of target-gas concentrations. For these applications, the response time becomes another important performance indicator (see Section 1.4).

Among different detection mechanisms, semi-conductor metal oxides (MOS) sensors (such as SnO_2 , WO_3 and NiO_2) are widely used. The mechanism of these sensors is based on decreasing the electrical resistance of the semi-conductor metal oxide in the presence of the desired gas. The main focus of many studies is to improve the characteristics of gas sensors in terms of selectivity, sensitivity, and response and recovery times (see Section 1.4 for the definition of these terms).

The main components of a MOS gas sensor are the sensing layer and the transducer which both affect sensitivity, and hence are important in the fabrication process [7]. Depending on the application, some ultra-sensitive gas sensors have been fabricated which can detect target gases with the accuracy of part per billion (ppb). Most MOS sensors include a heater which increases the temperature of the sensing layer during the measurement. Recently, room-temperature gas

sensors have been introduced which are a remarkable breakthrough in this area [8], [9]. In this chapter, background of MOS sensors, their components and sensing mechanisms, recent advancements and achievements in their fabrication processes, and their applications are introduced in detail.

1.2 Mechanism of sensing

Most metal oxides show remarkable sensitivity towards measurement of industrial and environmental gases including CO, CO₂, H₂, ethanol, acetone, and propane [10]. The sensing mechanism of a MOS gas sensor is as follows: a MOS sensor functions based on an alteration in electrical conductivity of the sensitive thin film as it is exposed to a target gas. When the thin film is exposed to the air oxygen molecules are adsorbed at the surface of the thin film. When the sensor is exposed to the target gas afterwards, oxygen molecules will be replaced by the target gas molecules at the surface of the sensing layer. This process leads to the alteration in resistivity of the sensitive layer which is a reliable parameter for measuring the concentration of the target gas.

The tendency of gas molecules to react with the semiconductor is a determining factor in the sensitivity of the sensor and can be explained by the band gap theory. Based on this theory, the probability of reaction between the target gas and semiconductor depends on the band gap in the reactants conduction bond and their electro negativity. The increase or decrease in conductivity depends on the type of majority of carriers in the semiconducting film and the nature of gas molecules as a donor or acceptor of electrons [11]. For *p*-type semiconductors, reducing gas (donor) decreases the resistance of the thin film, while oxidizing gas (acceptor) increases. These reactions are reversed for *n*-type semiconductors [5].

Following reactions show an example in which CO is detected. The adsorption of the oxygen atom to the surface of the sensing material surface is conducted as follows:

$$\frac{1}{2} O_2 \qquad \longrightarrow \qquad O^- + p^+$$
$$O^- + p^+ + CO \qquad \longrightarrow \qquad CO_2$$

The consequence of oxygen adsorption is the ionization of the oxygen atom, which creates a positive hole (p^+) . The adsorption mechanism is shown in Figure 1-1. After introducing a reducing gas (such as CO) to the sensor, a secondary reaction occurs between the ion, positive hole and reducing gas.



Figure 1-1 Schematic of adsorption of Oxygen molecules at the surface of metal oxide semiconductor thin film (reprinted from [11] with permission from © 2018 Science Letters Journal)

Depending on the temperature and electro negativity (tendency of an atom to make a shared pair of electron closer to itself) of the semiconductor, the probability of this reaction increases. The difference in the charge of the reactants is the main cause of the change in resistivity of the sensing layer which can be measured through the device. Depending on the semiconductor type and exposing gas, different oxygen species can be formed, as shown here:

$$O_2(gas) \longrightarrow O_2(ads)$$
$$O_2(ads) + e^- \longmapsto O_2^-(ads)$$
$$O_2^-(ads) + e^- \longmapsto 2 \ O^-(ads)$$

The alteration in conductivity of the semiconductor under vacuum and in the open air is shown in Figure 1-2. The current under vacuum condition is higher which depicts the resulting increase in the semiconductor resistance from oxygen adsorption on the surface of the thin film in the open air. These sets of reactions lead to the bending of the conduction band and formation of a temporary layer which is depleted as a result of the second reaction [12]. The schottky barrier is affected by the removal of the oxygen species from the surface of the semiconductor [13].



Figure 1-2 Conductivity of semiconductor under vacuum and in the open air. (reprinted from [13] with the permission from Elsevier)

1.3 Material selection

The main sensing component in the sensing layer of a gas sensor is the metal oxide semiconductor. Tungsten trioxide (WO_3) and Tin dioxide (SnO_2) are the most popular semiconductors in terms of cost, availability and compatibility for fabrication of MOS sensors.

1.3.1 Tungsten trioxide (WO3)

Tungsten has attracted much attention in recent years due to its wide band gap which is about 2.6 eV [14]. This *n*-type semiconductor can be found easily and in different forms such as tungsten wire, tungsten nanoparticles [15], Ammonium metatungstate hydrate (AMT) [16], and tungsten chloride (WCl6) [17]. The selectivity of WO₃ has been evaluated for different gases [18]. Among all the target gases tested, the highest sensitivity has been reported for acetone [19], NO₂ [20]–[22], H₂ [23], ethanol, and H₂S [24]. Also, the effect of Cr and Si doping using the flame spray pyrolysis deposition method (explained in Section 1.5.2.) for acetone detection has been studied widely [25], [26].

With a wide band gap which decreases the temperature dependence, high sensitivity is achievable at low temperatures (including room temperature) at which most electric devices are designed to be used [9]. WO₃ can be found stable at different crystal phases (from α to ε) for a wide range of temperatures [25]. The large surface to area ratio of WO₃ fibers also provides a larger surface reaction area for adsorbed target gas species. Also, after doping the WO₃ thin film with Cr nanoparticles, sensitivity of the composite structure is shown to be improved significantly [27]. However, the slow solubility rate of tungsten particles in some solvents at low temperatures [28] and the diameter of tungsten atoms leads to large particles, preventing the formation of narrow fibers [29]. The slow rate of solubility can cause a challenge in the use of this material for the

synthesis of a gas sensing layer. However, tungsten nanoparticles have been printed using inkjet deposition. Using this method, the average particle size and stability of nanoparticle suspension was found to be satisfactory (the particle diameters were measured to be 119 ± 3 nm (pristine WO₃), 118 ± 6 nm (Pt–WO₃), 109 ± 2 nm (Pd–WO₃), and 103 ± 16 nm (Ag–WO₃) [10]).

Tungsten oxide has been used in similar fabrication processes [30], [31]: tungsten oxide/PANI is used to fabricate a room temperature surface acoustic wave (SAW) NO gas sensor. The sensitivity of the SAW sensor is increased significantly after copper ion doping which enhances the detection limit to 1 ppb. A thin layer of Cu²⁺/PANI/WO₃ is deposited between the input and output interdigital transducers (IDTs) using the spin coating method. The covered area of the sensitive layer its thickness is reported as 1.5×1.5 mm² and 3000 A°, respectively. Sensitivity of the SAW sensor was tested by exposing the sensor to 20 ppb of NO. An acceptable response was achieved. The sensor response to O₂ at 150 ppm, NH₃ at 30 ppm, and CO₂ at 55 ppm was found to be insignificant [9]. Figure 1-3 depicts the porosity of a WO₃ crystalline grain after Cu doping followed by calcination at 250 °C.



Figure 1-3 SEM micrograph of the mesoporous Cu²⁺/PANI/WO₃ thin film calcined at 250°C for 5 h. (reprinted from [9] open access journal)

1.3.2 Tin dioxide (SnO₂)

Tin dioxide sensitivity (SnO_2) has been investigated towards several families of gases including ethanol, acetone, ammonia and carbon dioxide [32]. Also, due to suitable viscosity, SnO_2 can be electrospun to create the sensing layer. Also, SnO_2 has a wide band gap as a semiconductor and can be surface functionalized with different metals. These two are two important factors in increasing the sensitivity of the thin film layer [33].

Pure SnO₂ nanofibers have compact belt-like crystalline structures, which depending on the number of frequent calcinations steps can make unique morphologies suitable for ultrasensitive gas detection [34]. Fabrication of Fe-doped SnO₂ nanofibers using the spray pyrolysis method has shown a significant improvement in the response and recovery time [34]. Also, Pt loaded SnO₂ NFs has shown a high response time to 2.5 ppm of H₂ at 300 °C, and pristine SnO₂ has shown a remarkable response to 2.5 ppm of NO₂ at 150 °C [35].

The electronic interaction between the doping additive metal particles with tin oxide has been studied by Matsushima et al. [36]. The dispersion of Ag and Pd particles on the SnO₂ thin film surface changes the energy level of Sn 3d and O1s orbitals significantly. The binding energy of these orbitals in Ag (1.5 wt.%)-SnO₂ and pd(3.0 wt.%)-SnO₂ was found to be smaller (by 0.5 to 0.7 eV) than those of pure SnO₂. The band diagram of Ag-SnO₂ in oxidized and reduced state is shown in Figure 1-4. The difference in binding energy level of these two states is clear in this figure.



Figure 1-4 Schematic of the band diagrams of Ag-SnO₂ in an oxidized state (a) and a reduced state (b). (reprinted from [36] with the permission from © 1988 The Japan Society of Applied Physics)

1.4 Performance indicators

The performance of the gas sensor is a function of several parameters (which might have different names in different textbooks or articles). These parameters are including but not limited to:

Resolution (detection limit): the minimum concentration of the target gas that can be detected by the gas sensor.

Sensitivity: the change in the response as a function of the gas concentration, which is a criterion determining the precision of the sensor in detection of target gas.

Selectivity: the ability of a gas sensor to detect a specific specie among a mixture of gases.

Response time: the period of time from the exposure moment to reach the maximum signal [37].

Recovery time: the period of time from the drop in the maximum signal to the baseline.

Life cycle: the period that the sensor can operate non-stop [38].

Drift: saturation of the sensing layer by the target gas that decreases the sensing capabilities of the sensor.

Power consumption: the energy that is consumed by the sensor heater over time.

Dynamic range: the concentration range of the target gas that could be detected by gas sensor and is defined as the difference between the maximum and minimum detectable concentrations of the target gas.

1.5 Deposition methods

Deposition of the sensing layer on the electrodes is the most challenging step during the MOS sensor fabrication process. Among all the conventional methods, electrospinning, chemical vapor deposition, spray and flame spray pyrolysis have attracted attentions in the current studies. In the following sub-sections, the latest advances in the aforementioned methods are described.

1.5.1 Electrospinning

Electrospinning is a common method for deposition of polymer-based nanofibers. The most important advantage of electrospinning is the increase in the relative surface to the length ratio of crystalline structures which results in higher sensitivity of the thin deposited layer. An electrospinning setup requires three major parts: a high voltage supply, collecting surface and nozzle. In order to optimize the process, several key parameters (affecting the quality of the fibers) must also be controlled: Voltage, polymer solution parameters (which determine the diameter and morphology of nanofibers and must be carefully selected for a given application [39]) and ambient parameters (including temperature and humidity) [40].

9

Various types of metal oxides are successfully used in electrospinning, achieving diameter sizes in the order of nanometer. Zinc oxide nanofibers synthesized by electrospinning were found to be thermally stable at high operating temperatures up to 300 °C. The average diameter of nanofibers for this *n*-type semiconductor was characterized to be 150 nm. Large length to diameter and area to volume ratios of uniformly distributed nanofibers synthesized by electrospinning lead to a significant increase in sensitivity and reduced response and recovery time (to 3 s and 8 s, respectively). Transmission electron microscopy (TEM) image in Figure 1-5 shows the porosity and the large surface to length ratio of ZnO nanofibers [41].



Figure 1-5 TEM image of pure ZnO nanofibers. (reprinted from [41] with the permission from © John Wiley and Sons)

The average diameter of 200 nm has been obtained for WO₃ nanofibers using tungsten chloride (WCl6), which has shown the best performance at 500 °C operating temperature. For fabrication of such fibers, a voltage of 16 kV was applied between the collecting surface and nozzle located at the 15-cm distance from the collecting surface [17]. The formation of hollow porous SnO_2 nanofibers is performed using poly vinyl pyrrolidone (PVP) as the sacrificial template for multi-

step electrospinning. After decomposition of the PVP template in the temperatures around 300 $^{\circ}$ C, the Sn precursor will be exposed to air to form SnO₂ particles, where the Sn inside the core shell remains unreacted.

Metal oxides used in electrospinning can have improved sensitivity through calcination and doping. For instance, SnO₂ hollow nanofibers sensitive to ethanol has been fabricated by single capillary electrospinning followed by calcination at a wide range of temperatures.



Figure 1-6 Porous hollow SnO_2 nanofibers after calcination at 600°C. (reprinted from [42] with the permission of e-express polymer letters)

Figure 1-6 shows such nanofibers after calcination at 600°C. Studies using x-ray diffraction (XRD) has shown that Calcination in temperatures ranging from 300 °C to 600 °C results in higher intensity of SnO_2 nanofibers due to better crystallization, however diffraction peaks are created in temperatures above 400 °C as a result of discontinuity in the fiber's structure [42].

The effect of Yb doping on sensitivity and selectivity of the sensor is studied by exposing the sensor to different gases (methanol, ethanol, acetone, acetic acid, ammonia, dimethylformamide

(DMF), and acetic acid) at different concentrations. The best sensing performance was obtained based on 1 wt.% Yb-doped hollow SnO₂ nanofibers toward ethanol [43]. Also, binding energy for different orbitals of Sn (3d, 4d, 3p), O (1s) and Yb(4d) is measured by XPS spectroscopy. It is found that the lowest binding energy belongs to the adsorbed O⁻ and O²⁻ species on the surface of Yb-doped SnO₂ nanofibers which is a proof for enhancement in sensitivity of the sensor [44].

The gas sensing properties of Au-WO₃ nanofibers at two concentrations of Au (0.1M and 0.01M)has been studied toward volatile organic compounds (VOCs) such as n-butanol, methanol, acetone and ethanol among which the best sensitivity was recorded for n-butanol. Au functionalized WO₃ composite nanofibers was synthesized using AMT (Ammonium metatungstate hydrate) and polyvinyl alcohol (PVA) solution followed by a two-step calcination process at 600 °C. Au-WO₃ composite nanofibers were found to be more sensitive toward n-butanol with faster response (5 s) compared to that obtained using pure WO₃ nanofibers (31 s) [16]. Sensitivity and selectivity of WO_3 nanofibers towards acetone were enhanced by doping the sensing layer. Response of the WO₃ nanofibers to acetone for different dopant mass ratios is shown in Figure 1-7. It is shown that doping with 3% CO ions results in a sensitivity range required for detection of diabetes patients $(\geq 1.8 \text{ ppm of acetone})$ [45]. Another example of doping is the composite Pt-functionalized WO₃ hemi-tube nanofibers synthesized using PVA/ poly (methyl methacrylate) fiber-templating. SEM imaging of such a sensing layer has shown 52.5-nm thick WO₃ shell coated on sacrificial polymer layers (performed by multi-step electrospinning). Also, the size of Pt nanoparticles attached to the surface of hemi-tubes measured to be 3-7 nm [46].



Figure 1-7 (a) Responses of pure WO3, 1% CO–WO3, 3% Co–WO3, and 5% CO–WO3 nanofibers to different concentrations of acetone. (b) Response of 3% CO–WO3 nanofibers to 0.5–3 ppm of acetone for detection of diabetes. (reprinted from [46] with the permission from ©2018 American chemical society)

1.5.2 Spray pyrolysis

Spray pyrolysis is a simple and cost-effective method to fabricate gas sensors. Thin film deposition and composite film deposition can be done by spray pyrolysis. In this method, the solution is sprayed through a spray gun and nozzle on the substrate as a result of electrical potential difference between the nozzle and the substrate. The substantial components of the spray pyrolysis process are the atomizer, control mechanism, heater, solution and the substrate (see Figure 1-8).

Sensitivity behavior of SnO_2 -based gas sensors fabricated using spray pyrolysis has been studied as a function of the operating temperature [47]. Below the optimum temperature, gas molecules do not have enough kinetic energy to react with the oxygen molecules which are adsorbed at the surface of the sensing pallet. In the presence of a schottky potential barrier at low temperatures, the possibility of charge transport remains inadequately low. Although this method is simple, straight forward and cost-effective, there is no strong control on the thickness of the deposited layer and the crystalline size.



Figure 1-8 Schematic of a spray pyrolysis system

The optical and electromechanical properties of the indium doped zinc oxide thin layer deposited by spray pyrolysis are investigated. The temperature dependent behavior of deposition showed that the grain size becomes smaller as the temperature of the substrate is increased. The grain size of 100 nm and 70 nm with spherical shape was recorded at 450 °C and 500 °C, respectively [48],[49].

The effect of the air pressure, pyrolysis temperature, distance between the nozzle and substrate and solution viscosity on the deposited film thickness and grain size is studied. Based on these parameters, the layer can have a thickness of less or more than 20 nm with discontinuous or continuous shape, respectively. The size of the grain crystalline is directly proportional to the layer thickness, however the sensitivity has the opposite behavior and is inversely proportional to these two parameters [50]. Deposition and the film growth of the compact layer of tin oxide on a micromachined suspended membrane has also been investigated. The effect of the impact angle of deposited particles was observed and compared with the computer simulations [51]. The bottleneck in this process was found to be the etching of silicon for fabrication of the suspended membrane.

Zinc acetate and cadmium acetate were used to fabricate cadmium zinc oxide (CdXZn1-XO) by spray pyrolysis. The polycrystalline grain size was found to be inversely proportional to the concentration of zinc in the aquatic solution used for spray pyrolysis. The lower the concentration of zinc acetate the more the sensitivity toward hydrogen sulfide at relatively low temperatures [49].

Spraying the solution at high temperatures through a flame, which is the result of a combustion process, is a different fabrication method which is called flame spray pyrolysis. Spray pyrolysis at high temperatures causes phase evolution in semiconductors which leads to higher sensitivity toward target gases. Also, it can be used for deposition of single and multiple layers of thin film on the substrate [52]. As an example, an acetone detection sensor was fabricated using 10% Cr-doped WO₃ nanoparticles using the flame spray pyrolysis method. In 10% Cr-doped WO₃ composite structure, ε -WO₃ is the dominant phase which is not stable at room temperature. By calcinating the composite sensing layer up to 400 °C, phase transformation of dominant phase from ε -WO₃ to γ -WO₃ will occur [25]. Transmission electron microscopy (TEM) has shown that the average particle diameter in flame spray pyrolysis fabrication of WO₃ nanoparticles is about 20 nm. The lowest concentration of acetone which can be detected by this sensor was found to be 0.2 to 1 ppm with the response time of 10 s. This resolution covers part of the acetone detection range for diagnosis of Type I diabetes mellitus (T1DM) for which the acetone concentration is between 0.8 to 1.8 ppm.

Heat treatment process and the phase evolution in the dominant phase in the composite sensing layer can result in a significant increase in the sensor sensitivity. Also, the average primary particle size of the crystalline structure remains in the range of few nanometers. However, high temperature fabrication process may lead to inevitable damages to the substrate, including residual thermal stress in micron scales. For instance, the application of the flame spray pyrolysis in fabrication of embedded core particle systems has been investigated. The results have shown that depending on the interaction between the precursor and the metal at high temperatures the probability of significant losses in metal dispersion increases [53].

1.5.3 Chemical vapor deposition

Depending on the carrier gas and substrate temperature in the chemical vapor deposition (CVD) process, different crystal phases of tungsten oxide may be formed including α , β , γ , δ and ϵ [54]. Another version of CVD is localized aerosol-assisted chemical vapor deposition (AACVD) which is found to be a promising way to deposit nanoparticles into the sensing layer. The advantage of this method is high-rate deposition without the need for volatile precursors at intermediate temperatures. Localized heating of the substrate in the deposition area is another advantage of the (AACVD) method [55]. Also, only volatile and thermally stable precursors can be used for the conventional CVD; while AACVD is solution delivery based and wide range of precursors can be used. This feature of AACVD provides the mean to perform the entire process at a lower temperature. As a result, different types of substrates can be used including glass, silicon and even flexible polymers [56].

The use of AACVD for deposition of pure WO₃ nano needles (from W (CO)₆) at 500 °C has shown a significant decrease in the detection limit towards hydrogen. The results of experiments have shown that the fabricated sensor poses cross-sensitivity towards the ambient moisture [57]. This phenomenon might be due to formation of p-n junction in PdO-SnO₂ deposited by AACVD method (which prevents OH adsorption by the electron depletion layer) [58]. The integration of tungsten oxide nano-structures and nano-needles onto micro-machined transducers has been investigated. The results have shown a significant enhancement in sensitivity and the response time of non-aligned nano-needles towards H₂, H₂S, CO, C₆H₆ and NO₂ compared to quasi-aligned nano-needles and poly crystalline nano-structures. In addition to the arrangement of nano-needles, the diameter of the deposited structures was found to impact the performance of the sensor. Also, nano-needles with the diameters between 25 and 50 nm found to be more sensitive towards both oxidizing and reducing species [59].

Deposition of complex oxides such as Cobalt (II,III) oxide (CO₃O₄) and Cr_{2-c}Ti_xO₃ (CTO) using atmospheric pressure CVD seems to be an effective method to enhance sensitivity of these oxides towards target gases. This method increases sensitivity of the sensor by controlling the thickness of the deposited film and its micro-structure as compared to the hydrothermal processes functioning based on solid-state chemical reaction [60]. For instance, fabrication of CTO filmbased Cr_{2-c}Ti_xO₃ has shown high sensitivity towards ammonia and ethanol due to uniform distribution of titanium crystalline [61]. Also using PVA/PVP as the precursor polymer has found to increase the porosity of the sensing layer as compared to non-polymeric-based precursor solutions [62].

The effect of fluorine doping on Co_3O_4 nano-structures using plasma enhanced CVD has shown to provide great response and reversibility and also low working temperature (around 200 °C). Two different precursors were used in this study $Co(dpm)_2$ and $Co(hfa)_2$ TMEDA among which the second one provided homogeneous fluorine doped CaCO₃ sensing layer [63].

1.6 Applications

1.6.1 Medical applications

VOCs emitted by the human body have been used as biomarkers for early disease diagnosis. More specifically, the variations in VOC concentrations in breath or nasal air can be a non-invasive method of disease diagnosis. In the following sub-sections, the role of MOS sensors in disease diagnosis is discussed.

1.6.1.1 Diabetes

Non- invasive monitoring of exhaled breath in order to detect VOCs (such as acetone [27], [64] or isoprene [65]) is one of the most beneficial aspects of gas sensing technology. Identification and quantification of VOCs with high degree of accuracy has become possible using gas chromatography (GC) and mass spectroscopy (MS) [27]. The use of the exhaled breath for diagnosing diabetes mellitus (T1DM) has been studied in detail by Do Chau et al. [64]. Breath analysis techniques generally include classic tracers that provide infusion of stable or unstable gas molecules in the exhaled breath. Turner et al. [66] revealed that there is a specific correlation between the blood glucose level and exhale biomarkers in T1DM . They monitored the concentration of acetone in the breath versus the level of the patient blood glucose and found that T1DM is characterized by high acetone concentration.

Although GC and MS are considered as "gold standard" for detection of VOCs, they are bulky and required highly-skilled personnel. MOS sensors have been used to diagnose diabetes: e.g., an integrated breath collector in conjunction with a WO₃ sensing layer has been used in a handhold device. An elevation in the concentration of ethanol, ethylbenzene and methyl nitrate has been observed in the exhaled breath of T1DM [67]. For instance, the concentration of acetone in T1DM

patients is reported to be over 1.8 ppm [68]. Synthesis of functionalized NiO tubes with catalysts and nanofiber templating is another example of MOS sensors with high sensitivity to ethanol (as the T1DM biomarker). Or this sensor, a network of Pt-NiO-Pt tube was fabricated using electrospinning and calcinated in 600°C. Multi-layer coating of Pt, which was used as doping catalyst, in addition to frequent heat treatment leads to significant selectivity towards C_2H_5OH , H_2 and CO (Figure 1-9) [69].



Figure 1-9 Response of functionalized NiO sensor to different concentrations of H_2 , CO and C_2H_5OH . (reprinted from [69] with permission from Royal Society of Chemistry journal)

Ultra-sensitive acetone sensor is fabricated in a triple-step process by Xiao et al. [70]. They synthesized single crystalline porous ZnO nanosheets using calcination method. After preparing Pd nanoparticles, the surface modification process was performed by adding Pd nanoparticles into an agate mortar with ZnO nanosheets. The sharp peak in the x-ray diffraction results shows that

there is no impurity in the final thin film, and the Pd doped ZnO crystalline is deposited perfectly (Figure 1-10b) [71]. Figure 1-10a shows the SEM pictures of ZnO-Pd doped crystalline structures perfectly deposited as a thin film sensing layer. The crystalline size distribution is attributed to precision of the thin film deposition method and significantly affects sensitivity of the sensor.



Figure 1-10 (a) ZnO-Pd doped crystalline structure, (b) Sharp peaks in X-ray diffraction shows the pure crystalline structure as a result of successful deposition of ZnO-Pd doped layer (reprinted from [71] with permission from American Chemical Society)

1.6.1.2 Lung Cancer

In a study completed by Kischkel et al. [72], the VOCs in the breath of 15 patients with lung cancer were analyzed. Using gas chromatography (GC), a list of VOCs and their concentrations were compiled; notable gases identified were acetone, isoprene, and toluene. The results showed that the analysis of the variations of the concentrations of certain gases can lead to diagnosis of lung cancer. Again, GC is quite time consuming and expensive. Alternative methods of gas sensing can provide efficient, facile, and accurate measurement of different VOCs. Kim et al. [73] demonstrated a simple method for creating palladium functionalized tungsten oxide nanofibers for gas detection. The nanofibers were created by electrospinning a solution containing poly (methyl methacrylate) and tungsten ethoxide. After electrospinning, the composite nanofibers were
calcinated at 700°C, then the fibers were decorated with palladium by adding palladium to an ethanol/nano fiber solution, sonicated, and dried. Four types of sensing materials were produced pristine WO₃ nano-fibers, Pd-embedded WO₃ nano-fibers, Pd-nanoparticles/WO₃ nano-fibers and Pd-nano-particles/Pd-embedded WO₃ nano-fibers) and bound on top of the gold electrodes. These sensors were then exposed to H_2S and toluene in a high humidity environment to determine their performance and relevance to diagnosis of lung cancer. It was shown that the addition of palladium enhanced the sensors response to toluene. The produced sensors were able to show a response for concentrations as low as 1 ppm of toluene.

1.6.1.3 Cystic fibrosis and asthma

It has also been shown that asthma and cystic fibrosis alters the nitric oxide (NO) levels in breath and nasal air samples [74]. MOS sensors have been used to detect NO using various surface topographies and chemical compositions. Samples were taken from 19 healthy children, 36 children with asthma, and 8 children with cystic fibrosis. The results of the oral-exhaled breath showed that asthmatic patients who were treated with no or low doses had an increased amount of NO compared to those without asthma (13.8 ppb versus 4.8 ppb). However, little changes of NO were detected for children with cystic fibrosis, showing a concentration of 5.8 ppb. In contrast, using nasal-exhaled breath showed larger changes in NO concentrations for patients affected by cystic fibrosis compared to the healthy control group, 9-15 ppb and 21 ppb respectively. The concentration of NO for asthmatic patients showed lower variations at 27 ppb.

In a study conducted by Kannan et al. [75], MOS sensors were fabricated using In_2O_3 thin films and promoters to sense low concentrations of NO_x . These sensors were shown to be responsive to a low concentration of 5 ppm with moderately high response. Further experimentation with reaction promoters like gold and titanium oxide (TiO) showed that the response of the newly fabricated sensors increased. Although the tests were only completed using a concentration of 25 ppm NO_x it can be concluded that the trends tend to look similar at lower concentrations. Current MOS sensors do not generally show a good response when they are exposed to very low concentrations (ppb levels) required for disease diagnosis. However, new advances in fabrication processes will result in the development of MOS sensors that can be used as accurate and non-invasive methods for disease diagnosis.

1.6.2 Environmental applications

In today's society a majority of the world's population spends most of their lives in highly populated, urban areas. This exposes us to a large amount of hazardous gases from manufacturing plants, vehicle emissions, and many other sources that can affect the human body and the global climate. For example, VOCs such as hydrogen sulfide (H₂S) and methane (CH₄) are harmful at high concentrations. Thus, it is important to develop technologies that can analyze and detect their concentrations as efficiently and accurately as possible.

1.6.2.1 Lethal gases

Hydrogen sulfide is a highly corrosive and toxic gas that can cause fatality. Exposure to a dose of >500 ppm causes death in less than a few minutes [76]. However, a short-term exposure to H₂S at concentrations lower than 100 ppm is safe for humans. H₂S can be found in many industries such as sewage treatment, petroleum refining [76], farm slurry treatment [77] and production of rubber chemicals [78]. It is estimated that 125,000 UK workers are exposed to H₂S [79], for this reason there have been heavy emphasis on H₂S detection to ensure a safe environment.

A highly-sensitive H₂S sensor was fabricated using single crystal In₂O₃ whiskers, enabling the detection of H₂S (at a ppb level) at room temperature [80]. This fabrication method involved growing the sensing material, In₂O₃, by placing indium balls or a mixture of indium oxide and graphite in a quartz tube and heating it to 1050-1100°C. It was found that whiskers with a diameter of approximately 100-300 μ m grew at the indium source and nanowires/bipyramids were deposited on the quartz tube. To fabricate a sensor using the single crystal whisker, a single whisker was placed on a substrate and leads were attached to it using gold paste. The whisker sensors were able to detect 200 ppb of H₂S at room temperature and saturated at 10 ppm. At low concentrations, the response and recovery times were rather quick, 2-3.5 min for 200-400 ppb of H₂S. However, at high concentrations (10 ppm) the response time was quick, 1-4 min, but the recovery took 2 hours.

As another type, the nano-bipyramid sensors were fabricated by soaking the bipyramids in methanol, sintering at 400°C and painting a thick film on alumina substrates with gold pads. In contrast to the whisker sensors, the bipyramid gas sensors showed a lower response time even at high H₂S concentrations. This type of sensors kept a stable response time over a range of gas concentrations (2 min for 20 ppm and 2.5 min for 80 ppm). However, the recovery time increased dramatically from 20 min for 20 ppm to 1.3 h for 80 ppm.

Recent developments in gas sensing technology have led to simpler methods of fabricating sensing material that can be used within the working concentrations. Chang et al. [81] developed a gas sensor using CuO doped SnO₂ nanofibers to detect 1-100 ppm of H₂S. The electrospinning fabrication technique was used to create the hollow nanofibers. Poly vinyl pyrrolidone (PVP) was used as the fibrous scaffold which was mixed with a solution containing tin chloride and copper (III) chloride to create the precursor solution. The solution was then electrospun to create

nanofibers. After doing, the fibers were placed in an oven to dry and then calcinated at 600°C. Calcination at high temperatures allowed all organic matter and PVP to oxidize and decompose, leaving only metal oxide crystal grains. It was shown that the optimal sensing material for H₂S detection was SnO₂ doped with 5 mol% of CuO at a sensing temperature of 330°C. The response and recovery times for this sensor were quite low, 5 s and 12 s, respectively. Also, this sensor was able to sense H₂S at concentrations ranging from 1 - 100 ppm.

1.6.2.2 Combustible gases

Methane is a combustible gas that poses high risk especially in the mining industry where digging can release methane deposits that may combust given the right conditions. In addition, methane is one of the most impactful greenhouse gases that is emitted every day. Being able to measure the concentration of methane in the environment is both safety environmental concerns.

A highly-selective methane sensor was fabricated by Zhang et al. [82] using a nickel oxide (NiO) and reduced graphene oxide (rGO) composite sensing film. To fabricate the sensor, hydrothermal synthesis of NiO nanoparticles was conducted using an autoclave and a thoroughly stirred solution of nickel chloride hexahydrate, sodium oxalate, polyethylene glycol, and ethylene glycol. This process resulted in NiC₂O₄ precipitate that was then calcinated at 400°C to produce NiO nanoparticles. The next step involved autoclaving the NiO with graphene oxide; after centrifugation and multiple rinse cycles NiO/rGO samples were obtained. This solution was then coated onto a ceramic tube to form a thin film with gold electrodes at either ends of the tube. This sensor showed an operating range of 100-500 ppm and showed low response and recovery times of 6-18 s and 16-20 s, respectively. In addition, when this sensor was exposed to different gases at

1000 ppm it showed significantly higher responses to methane and lower response levels to other gases like CO₂ and CO.

1.7 Motivations

The commercial MOS sensors have housing around them. The presence of the housing makes the gas diffusion process (towards the sensing layer) slower and hence damping the response of the sensor. This problem is even more critical in lower concentrations of VOCs (important for disease diagnosis). Taking the housing off is a time-consuming process with a high failure rate (depending on the method that is used to take the housing off, the sensor connections are damaged which results in malfunction of the sensor). Fabrication of a sensor with similar capabilities that also does not need a housing will be cost- and time-effective. In addition to this need, the performance of such sensors can be optimized toward a target gas. In this thesis, it is desired to fabricate a sensor for detection of tetrahydrocannabinol (THC, the psychoactive element in cannabis) which is not commercially available. To enhance selectivity of the sensor towards THC, a microfluidic-channel will be combined with the sensor (see Section 1.8). Integration of the sensor in the microfluidic channel is another motivation for in-house fabrication of MOS sensor, as the commercial sensors housing needs to be removed.

1.8 Objectives

In this research, the fabrication process of a tin oxide (SnO_2) /Poly ethylene oxide (PEO) gas sensor using electrospinning method is presented. Sensitivity enhancements towards methanol and THC molecules using calcination and gold doping techniques are investigated. The gold doping of the composite nanofibers is performed by a sputtering machine. The performance of the sensor with different doping thicknesses, including 5nm, 10nm and 15 nm, as well as different calcination temperatures, ranging from 200°C to 400°C, is investigated in order to fabricate MOS sensors with high sensitivity.

Another objective of this research is the implementation of the fabricated gas sensor in microfluidic channel that has shown to enhance the selectivity of the MOS sensors [83]. The microchannel with different combination of coatings increases the selectivity of the sensor towards particular VOCs. Finally, a feature extraction model is used to segregate the results of THC and methanol tests in a 3D space.

1.9 Thesis Outline

In Chapter 1, a detailed literature review including recent advances in fabrication of MOS sensors (using electrospinning, chemical vapor deposition and spray pyrolysis methods) was conducted. Also, MOS sensor medical and environmental applications were presented

In Chapter 2, the fabrication process of the gas sensor substrate is clearly explained. The deposition process of the sensing layer and the construction of the experimental setup are also described.

The characterization and performance optimization of the gas sensor by calcination and sputtering methods are described in Chapter 3. Additionally, the results of the tests for thin film deposition method are concisely presented.

After fabrication and characterization of the sensor, results of the tests with different concentrations of methanol and mixtures of methanol/THC are presented in Chapter 4. This chapter also includes test results of the embedded sensor in a microfluidic channel and feature extraction analysis of the results.

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Finally, conclusions and future prospects of sensor fabrication using the electrospinning methods are presented in Chapter 5.

Chapter 2: Experimental setup and device fabrication

In this chapter, fabrication and testing processes used for the development of MOS gas sensors are explained in detail. In essence, these processes include three major steps (see Figure 2-1): the first step consists of material selection, microfabrication and miniaturization of the substrate. The second step involves characterization of the sensing layer and optimization of the parameters that enhance the performance of the sensor. Implementing the sensor inside the microchannel with specific coatings in order to make it selective to specific target gases is the last step of fabrication. Comparison of the test results across different VOCs before and after embedding the sensor inside the microchannel is necessary for the segregation of different gases by using the feature extraction model. Finding the patterns that are common between different concentrations of the same analyte is the main objective of the feature extraction model.

Material selection and microfabrication

- Developement of IDEs and microheater
- Development of sensing pallet
- Miniaturization of the sensor

Optimization and charactrization

- Optimization of the electrospinning parameters
- Gold sputtering of the sensing layer
- Heat calcination of the sensing layer

Microchannel and feature extraction

- Testing the sensor against different VOCs
- Implementation of the sensor inside the microchannel
- Feature extraction of the results in 3D space

Figure 2-1 three main steps of gas sensor fabrication conducted in this study.

The relation between the steps one and two is shown in Figure 2-2. This figure shows that the microfabrication process includes many iterative processes involving different steps that are dependent on each other. Characterizing the surface morphology by SEM and testing the sensor after any modifications is a part of the fabrication process.



Figure 2-2 Relation between different steps of the microfabrication process

In the following sections, material selection and the micro-fabrication methods used (i.e., electrospinning and thin film deposition) as well as the setup built in-house are described.

2.1 Microfabrication

Metal oxide semiconductor gas sensors include three main components: substrate, interdigitated fingers and the sensing pallet (Figure 2-3). Using glass slides as substrate is the first option since they are economical and available in different thicknesses. It is also possible to fabricate an array of sensors on a glass slide and then cut it into small pieces.



Figure 2-3 Schematic of main components of a MOS gas sensor

Thermal conductivity (K) and thermal expansion coefficient (α) of the substrate are the two determining factors in the selection of the substrate. In this thesis, initial attempts towards the fabrication of interdigitated fingers were done on a glass substrate. The active sensing area dimension was chosen as 1cm×1cm and the gap size between the electrodes varied between 50 to 200 µm (Figure 2-4). However, these attempts failed: the heater (see Figure 2-5) fabricated on the substrate on the opposite side of the interdigitated electrodes (IDEs)) could not be fabricated and used for high temperatures as the glass substrates deformed. The role of the heater is important since the intermediate or high temperatures facilitate the sensing process (increasing the sensor temperature from the room temperature to 200°C and higher improves the sensor performance drastically [84]). As a result, silicon wafer substrates have been used instead to improve the thermal properties of the sensors.



Figure 2-4 Fabricated interdigitated fingers on a glass slide

Besides the high temperature, the dimension of the sensing area affects the performance of the sensor. The smaller the dimension the faster the sensing reactions. The small sensing area also decreases the amount of power that is required to keep the substrate at a constant temperature. Therefore, the original sensing area $(1\text{cm}\times1\text{cm})$ was changed $5\text{mm}\times5\text{mm}$. For fabrication of IDEs with this dimension on a silicon wafer, first the substrate was cleaned with piranha solution, rinsed with DI water, and then dried using clean compressed air. The, a 35-nm chromium layer followed by a 65-nm gold layer was sputtered at a rate of 1 A°/sec. The S1813 photoresist solution (purchased from Sigma-Aldrich) was then spin coated at 2000 rpm for 30 sec, resulting in a 2- μ m layer. This thickness was determined based on the photoresist material and the speed of the spin coater (see Figure 2-6). Then, the photoresists film was cured on a hot plate at 115 °C for 60 seconds (see Table 2-1). To pattern the interdigitated electrodes, the masks were designed in a way that the 100- μ m fingers were placed at a 20- μ m gap Figure 2-7(a)). To transfer the patterns, UV light was illuminated on the masks. Then, the exposed regions (corresponding to transparent areas

on the mask) were washed out by immersing the substrate into photoresist remover. The same procedure was performed on the back side of the silicon wafer to fabricate the micro-heater as illustrated in Figure 2-7(b). Subsequently, the gold and chromium layers on the exposed and removed regions were etched by immersing the substrate into the gold and chromium etchants. Figure 2-8 shows an array of interdigitated fingers fabricated on a silicon wafer with a 2-inch diameter. Finally, the chips were immersed into the photoresist remover, and the silicone substrate was cut into $5 \times 5 \text{ mm}^2$ pieces using a laser micro miller (see Figure 2-8).



Figure 2-5 Mask designed and use to fabricate the chip of (a) heater and (b) IDEs on silicon wafer substrate

Table 2-1 Process condition for S1813 photoresist on silicon substrate using different devices

Hotplate	Oven
115 C	150 C
60 sec	60 sec



Figure 2-6 Spin Speed Curve for Dow S1800 Products (reprinted from Dow[®] S1800 series Positive Photoresist catalog)



Figure 2-7 The micro-fabricated patterns on (a) top – interdigitated fingers, and (b) bottom – micro heater.



Figure 2-8 Array of fabricated (a) interdigitated fingers and (b) micro-heaters on the silicon wafer chip

2.2 Solution preparation

The precursor solution used for the MOS sensor mimics that of León et al. [85] consisted of a solution of SnCl₄, poly (ethylene oxide) (PEO), deionized (DI) water, isopropanol, 1-propanol, and chloroform (CHCl₃) (all purchased from Sigma-Aldrich). SnCl₄, DI water, propanol, and isopropanol were first mixed at a molar ratio of 1:9:9:6. For this study, multiple variations of this solution were made and tested. These variations have shown different performances (see the summary of the results in Chapter 3). Each solution was made by first magnetically stirring a mixture of DI water, propanol, isopropanol, and SnCl₄ for 2 h and then sonicated for 30 min to ensure a high quality of tin chloride. Then, a solution of PEO/CHCl₃ was mixed with the ratio of 100mg to10ml, respectively. The two solutions were then mixed together and magnetically stirred for another 30 min.

As mentioned above, a series of different solutions were made and tested to find the optimum concentrations of the solvent and solute. To increase the sensitivity of the sensing material, first the amount of semi-conductive material was increased. This solution (seen in Table 2-2) was found

to have low viscosity (due to the high ratio of PEO) resulting in a very slow extrusion rate during the electrospinning process. For the second solution, the amount of SnCl₄ was increased while decreasing the amount of PEO at the same time. This turned out to work very well in terms of viscosity and resulted in deposition of nano fibers. Using the same amount of PEO, the amount of SnCl₄ was increased once again which resulted in disjointed fibers as the amount of the carrier polymer was not sufficient. Therefore, it was concluded that the second solution is optimum for electrospinning.

Table 2-2 Different proportions of solutes and solvents made and tested to find optimum values corresponding to the highest sensor performance

Solvant	Amount	Solute	Amount	
H ₂ O	2 ml	SnCl ₄	0.5, 1 & 2 gr	
CHCl ₃	5 ml			
Isopropanol	0.75 gr	PEO	150 mg	
1-propanol	0.5 gr			
H ₂ O	2 ml	SnCl ₄	0.5, 1 & 2 gr	
CHCl ₃	5 ml			
Isopropanol	0.75 gr	PEO	300 mg	
1-propanol	0.5 gr			

2.3 Test setup

For testing the fabricated sensors a 1 liter chamber with transparent walls was built (see Figure 2-9). The chamber walls were cut using the water jet and glued together by the epoxy glue. Using epoxy glue ensures that the edges are perfectly sealed. Data acquisition was performed using a Pasco box. To be able to read the current change in the sensor, a 1 k Ω resistor was placed in series with the sensor in the circuit. The voltage across the resistor in series was recorded through the Pasco box. Data was collected with the frequency of 10 samples per second.



Figure 2-9 Schematic of the test setup including the test chamber and the sensor (placed inside it), electrical circuit and display.

2.4 Electrospinning setup

Electrospinning is a widely-used technique for creating polymeric micro/nanofibers using a high voltage electric field. This process works based on the principle of high electrical forces as compared to surface tension forces. The elements of an electrospinning setup include a high voltage power supply, a pipette/syringe tip, and a grounded collector plate. The polymer solution is drawn into a pipette/syringe, and the power supply is connected to the collector plate and the syringe/pipette tip as shown in Figure 2-10. Once a voltage is applied, an electric field is produced between the nozzle and the collector to create the polymeric fibers. In this process, there are several parameters that can affect the quality and size of the fibers. These parameters include: the concentration and viscosity of the solution, the flow rate of the solution, the voltage applied, the distance between the collector and the nozzle, and the ambient temperature [86]. These parameters make electrospinning a highly versatile tunable process.



Figure 2-10 Schematic of the electrospinning setup

In this thesis, an electrospinning setup was built (see Figure 2-11). This station is equipped with a high voltage power supply (Gamma high voltage device), a syringe pump, an adjustable z-axis table, perimeter cage, and a microcontroller operated safety system. The high voltage power supply produces the electric field that is required to produce different types of fibers. The syringe pump

is used to extract the polymer solution from the syringe with a metallic needle attached to its end. Those two pieces of equipment are essential to the electrospinning process, however to provide more versatility and safety during the fabrication process other components were designed and included in the setup as explained below.





One of the factors that can affect the quality and characteristics of the fibers is the distance that the collector plate is located from the tip of the needle. For this reason, an adjustable z-axis table was added underneath the syringe pump. This was also added for the situations where the system needs to be in operation for a long period of time to create a thicker polymer fiber mat. The prolonged operation of this system is also the reason for designing a casing around the major components so that the system can be left unattended for longer durations without causing potential danger to others. The casing is also properly ventilated as some solvents used to make the polymer solution

can be harmful or have an unpleasant odour. Also, to prevent others from opening the case and potentially shorting the system (and electrocuting themselves), a safety switch was installed in the door of the casing. This safety includes: a Hall effect sensor, a microcontroller, and an AC power adapter. The safety schematic can be seen in Figure 2-12; the Hall effect sensor will sense whether or not the door is closed at which point it provides an input to the microcontroller to allow the power to reach the high voltage power source. So, if the door is open and easily accessible to something that can be harmed the high voltage power source will not turn on.



Figure 2-12 Schematic of the safety system for electrospinning setup

2.5 Fabrication of thin film

Another process used to fabricate MOS sensors (in addition to electrospinning) is thin film deposition on the same substrate described earlier. In this thesis, a thin film was casted by extruding the solution through a needle and onto the substrate using a syringe pump. After placing the liquid on the substrate, the evaporation phase starts. This phase includes cold and hot evaporation at room

temperature and on the hot plate, respectively (see the parameters in Table 2-3). At the end of this phase, tin dioxide and the precursor polymer form a crystalline structure on top of the interdigitated fingers.

Evaporation phase	Heat treatment
Cold evaporation	25°C, 24hrs
Hot evaporation	100°C, 2hrs

Table 2-3 Time period and temperature of each step in evaporation phase

The MOS sensors fabricated through the thin film and electrospinning deposition are compared in Chapter 4 to find the method that produces a higher performance sensor. The method chosen will be further optimized to increase the sensor sensitivity (compared to that of the commercial sensor).

Chapter 3: Characterization and optimization of sensing layer

The first objective of this chapter is to compare the performance of the fabricated sensors by electrospinning and those using the thin film deposition method. High temperature calcination and gold catalyst functionalization of the sensing pallet, improving the performance of the sensors, are also highlighted in this chapter. Results of the sensitivity towards methanol tests in addition to surface morphology images taken with SEM are presented for each improvement.

3.1 Optimization of solution parameters

To optimize the solution viscosity for the deposition process, the proportion of each chemical needs to be optimized. Table 3-1 lists the percentage composition (mass ratio) of each element in the fabricated layer of the deposited samples on the crucible sample holder. Obviously by increasing the mass ratio of tin in the solution, its percentage composition increases in the deposited layer correspondingly. The other important factor in the selection of the optimum solution is the quality of nanofibers after electrospinning. The desired sensing pallet contains the best quality of nanofibers with the maximum amount of tin element. The amount of polymer that is used to prepare the solution determines the viscosity of the samples. A viscous solution increases the chance of short circuit during the electrospinning process. On the other hand, using a low viscosity solution does not lead to formation of nanofibers.

| Spectrum |
|----------|----------|----------|----------|----------|----------|----------|
| Label | 1 | 2 | 3 | 4 | 5 | 6 |
| С | 24.11 | 19.56 | 22.35 | 19.48 | 18.63 | 21.43 |
| 0 | 4.32 | 4.59 | 10.29 | 8.17 | 10.2 | 4.36 |
| Al | 45.03 | 38.47 | 4.71 | 9.75 | 4.28 | 0.35 |
| Si | 0 | 1.44 | 0.24 | 0.22 | 0.27 | 0.19 |
| Cl | 12.31 | 15.64 | 28.24 | 29.17 | 30.82 | 27.75 |
| Sn | 14.24 | 20.29 | 34.18 | 33.21 | 38.8 | 45.93 |
| Total | 100 | 100 | 100 | 100 | 100 | 100 |

Table 3-1 Percentage composition of each element in the deposited layer for six different solutions described in Chapter 2

The element analysis imaging depicts different elements that exist in the fabricated layer graphically. Tin (Sn) nano particles can be detected in Figure 3-1 (b and c) with purple color. The purple pixels in this picture proves that tin is scattered all over the fibers. The peaks in the graph (Figure 3-1a) compares the percentage composition of different elements. Chlorine (Cl) and tin (Sn) have the highest concentration among all the elements due to the amount of tin (IV) tetrachloride (SnCl4) that is used for preparing the solution. Figure 3-2 shows the SEM images of the nanofibers that are deposited suing the solutions that were introduced previously in Chapter 2. Based on the SEM images solution number 2 and 3 (see Table 2-2) lead to the best quality on nanofibers with the maximum surface to volume area. Using the same amount of semiconductor material, as the nano fiber's diameter decreases the more surface area is obtained.



Figure 3-1 (a) the element analysis of the images of nanofibers, and (b) tin (Sn) structure that has been successfully deposited can be seen in purple color

3.2 Thin film deposition

The sensor fabricated by thin film deposition method before and after heat treatment is shown in Figure 3-3 (a) and (b). SEM images (Figure 3-3 (c) and (d)) show the crystalline structure of the thin film layer that is totally different than the nanofiber structures. Heat treatment at 100°C for 2 hours leads to the growth of the crystalline structure and increases the active surface area of the sensing pallet which is the platform for the gas sensing reactions.

The sensing layer that is fabricated through the thin film deposition is thermally unstable. Increasing the heat treatment temperature or also sensor operating temperature to intermediate temperatures (~ 200° C) leads to formation of discrete island shape zones inside the sensing pallet. The crack initiation starts at 150°C (Figure 3-4(a)) and becomes more visible at 200°C (Figure 3-4(b))



Figure 3-2 SEM images of the deposited nanofibers by electrospinning method for six different mass ratios of the contents introduced in Chapter 2



Figure 3-3 Fabricated sensor by thin film deposition before (a) and after (b) heat treatment. SEM images of the sensing layer before (c) and after (d) heat treatment



Figure 3-4 Formation of discrete zones in the sensing pallet due to thermal instability at intermediate and high temperatures

The voltage response of the two sensors fabricated through an identical process (i.e., heat treatment at 100°C) are compared against a commercial MOS sensor (Figaro – TGS 2620) for 1000 ppm of methanol (Figure 3-5) .The magnitude of the signal obtained for the fabricated sensors is significantly less (approximately 80% less) than that of the commercial sensor. Since the thin film structure is thermally unstable at high temperatures, calcination of the thin film at temperatures above 200°C does not improve the sensitivity of the sensor. On the other hand, electrospun nanofibers have the capability of being calcinated at high temperature to improve their sensitivity towards a specific target gas. Therefore, in this thesis, the attempts are towards the characterization and improvement of the MOS sensors fabricated through electrospinning.



Figure 3-5 Comparison of the sensor responses of the two thin-film deposited sensors (fabricated through an identical process) with that of a commercial sensor (Figaro – TGS 2620) for 1000 ppm of methanol

3.3 Calcination of electrospun nanofibers

High temperature calcination of both thin film layer and nanofiber layer increases the porosity of the sensing pallet. Porous sensing layer facilitates the oxygen adsorption reaction at the surface of tin crystalline and nanofibers by increasing the surface roughness and creating snowflake shape concavities. The calcination temperature plays a vital role in the enhancement of the sensor sensitivity. The calcination temperature starts from the sensor operating temperature and goes up to 400-450°C. The other factor that influences the sensor sensitivity is the calcination period. Cyclic heat treatment at an intermediate temperature is another calcination method based on the literature [87]. The response of the fabricated MOS sensor before and after calcination has been tested. The calcination period in the oven was performed for 4 hours for different calcination temperatures including 250°C, 300°C, 350°C and 400°C. The fibers after calcination tend to be

more transparent (see the SEM images in Figure 3-6) due to the change in electron absorption properties of the sensing layer.



Figure 3-6 SEM pictures of the sensing layer after calcination for four hours at (a) 300°C and (b) 400°C

The response of the sensors with different calcination temperature towards 1000 ppm of methanol are presented in Figure 3-7. The optimum calcination temperature found to be 350 °C due to higher sensitivity of the sensing layer towards methanol. For the calcination temperatures above 350°C, the texture of the fibers will get damaged and affects the performance of the sensor.

3.4 Gold doping

A widely-used method for increasing sensitivity and selectivity of MOS sensors is doping [88-90]. The performance enhancement based on doping is highlighted in a study completed by Xiang et al. [91]. They doped ZnO nano-rods with silver (Ag) nano particles. Their study also demonstrated the effectiveness of doping by exposing the doped nanorods and bare nanorods to 10 ppm of ethanol at different working temperatures. It was shown that at all temperatures the doped nanorod sensor has a higher response compared to the sensor without doping. This phenomenon is explained by Yamazoe et al. [92]; in essence, the noble metals increase the rate of oxidation due to their catalytic properties. The challenging part is to find an effective doping method that can be used to introduce the dopants to the sensing material. Several methods have been used such as: mixing [93], dip coating [94], and RF-magnetron/reactive DC sputtering [95].



Figure 3-7 Response of the sensors with different calcination temperatures to 1000 ppm methanol

In this research, gold doping of the sensing layer is performed by sputtering an ultrathin layer of gold on top of the semiconductor sensing layer. To ensure no contact between the gold electrodes and the ultrathin gold doping layer, an adequate amount of semiconducting material is placed

before sputtering. The DC sputtering of gold (Au) is used to enhance the performance of electrospun SnO₂ calcinated nanofibers. The ultrathin gold sputtered layer has been achieved for three different thicknesses including 5nm, 10nm and 15 nm to find the optimum thickness. Figure 3-8 depicts the SEM image of a electrospun SnO₂ calcinated nanofibers doped with a 10-nm gold layer.



Figure 3-8 SEM image of 10 nm gold doping of electrospun nanofibers (SEM MAG: 500x)

Figure 3-9 shows the responses of the sensors doped with three different thicknesses (5nm, 10nm and 15 nm). The sensors were exposed to 1000 ppm of methanol and the results show that 10-nm gold doping produces a higher response. For the gold thicknesses more than 10 nm, the gold percentage composition inside the sensing layer becomes more dominant and as a result conductivity of the sensing layer increases. Therefore, the sensing layer electron absorptivity – the determining factor for the sensor to adsorb more target gases – slightly decreases. Figure 3-10 presents the SEM images of 5 and 10 nm gold doping of the sensing layer.



Figure 3-9 Test results of sensors with different thicknesses of deposited gold to 1000 ppm of methanol



Figure 3-10 SEM images of (a) 5 nm and (b) 10 nm gold doped nanofibers (SEM MAG: 2000x)

After finding the optimum calcination temperature and gold doping thickness, the combined effect of these characterization methods is assessed by cyclic exposure of the sensor to 1000 ppm of methanol. As it is shown in Figure 3-11, the effect of calcination is more dominant compared to gold functionalization. Combination of doping and calcination has the highest sensitivity towards methanol due to their synergetic effects: porosity of the nanofibers combined with the presence of gold particles, facilitates the adsorption of oxygen at the surface of the semiconductor. Diffusion of the target gas molecules into the sensing pallet (that has become a 3D structure after gold sputtering) makes the recovery step slower and causes a raise in the response during the last cycles of the exposure.



Figure 3-11 Effects of calcination, doping and calcination-doping on the response of the sensor to 1000 ppm of methanol

3.5 Sources of noise

The sensor resistance is the average of the random network of resistances that each element of the sensing pallet experiences due to temporary surface adsorption of an analyte. Furthermore, the surface temperature of the active sensing area is attributed to the micro heater power consumption as well as atmospheric conditions. Depending on the local temperature distribution of the sensing layer, the rate of adsorption and release reaction changes. This set of alterations results in corresponding changes in the resistor and output voltage of the sensor (See thick graphs in Figure 3-11).

Ambient relative humidity and its variations can also cause a significant shift in the sensor resistance. Water vapor molecules can have amplification or mitigation effects on the sensor's output voltage [96]. If the water molecules reduce the semiconductor, they amplify the response to reducing gases and diminish it to oxidizing gases.

Chapter 4: Results and discussion

In this chapter, the test results of the fabricated sensor towards different concentrations of VOCs, including methanol and a mixture of methanol and THC are presented. Additionally, the effect of initial drift cycle that decreases the magnitude of the signal is investigated. Later on, the effect of the microfluidic channel on the selectivity of the gas sensor towards THC is investigated and compared to the results obtained from a commercial MOS sensor. Segregation of the results in a 3D space using the feature extraction is also presented.

4.1 Testing sensors against different VOCs

Based on the material that is used for deposition of the sensing pallet, the response of the sensor varies across different volatile organic compounds (VOCs). Every single combination of the metal oxide semiconductor and carrier polymer has a unique response to a particular concentration of a target gas. These unique responses are expected to be different in terms of the response and recovery times and the magnitude across different VOCs. In this thesis, the performance of the sensor with respect to **methanol** and a mixture of **THC/methanol** has been investigated. Methanol is a biomarker for different functions in the human body and even a slight change in the concentration of this biomarker from the normal range in the exhaled breath can be a sign of possible body malfunction. The THC molecule is the psychoactive element in cannabis that exists in the exhaled breath of Marijuana consumers. The concentrations that are used for performing the tests are 200ppm, 400ppm, 600ppm, 800ppm and 1000 ppm.

Figure 4-1 shows the cyclic response of the fabricated sensor to different concentrations of methanol. The response of the sensor to different concentrations seems to be reproducible.

Additionally, the response and recovery times are considerably fast. The presence of the systematic noise can be obviously observed in all of the graphs. Repeated simultaneous adsorption and desorption at the surface of the semiconductor is the main reason of this systematic error. This is due to the fact that the output voltage of the sensor is directly related to the number of target gas molecules that are absorbed onto the surface of the semiconductor. Furthermore, the oxidization and reduction reactions that occur solely as a result of humidity, make the sensing pallet chemically unstable.



Figure 4-1 cyclic response of the sensor to 200,400,600,800, 1000 ppm of methanol

The response of the fabricated sensor to different concentrations of the mixture of methanol/THC is slightly higher than its response to corresponding concentrations of pure methanol (Figure 4-2). This phenomenon explains the higher sensitivity of the fabricated sensor towards THC molecules compared to methanol. The difference in the magnitude of the responses to methanol and mixture of methanol/THC is solely attributed to the selectivity of the sensor towards THC molecules.



Figure 4-2 cyclic response of the sensor to 200,400,600,800, 1000 ppm of mixture of methanol and THC
The sensing area of a MOS sensor is always in a drift phase. The drift phase is defined as the saturation phase of the sensing layer with the target gas over time. This leads to an infinitesimal voltage drop over time. The intensity of the drift phase is much higher at the beginning of the sensor usage. In order to resolve this issue the sensor should be connected to a power supply over night for a couple of days until the voltage drop across two consecutive days becomes negligible. This process is called the "conditioning phase". Figure 4-3 presents the response of two sensors to 1000 ppm of methanol over 5 consecutive days. A significant voltage drop is observed in the first three days. However, the signal that was obtained on the fourth and fifth days was stable. Also the sensor warm-up time can vary with the atmospheric condition. Humidity is the most important environmental factor that affects the warm-up and conditioning phase of the sensor. The warm-up phase gets infinitesimally shorter after each usage of the sensor



Figure 4-3 Responses of two fabricated sensors (a and b) to 1000 ppm of methanol over five consecutive days during the conditioning process

4.2 Implementation of the fabricated sensor inside a microfluidic channel

It has been shown [97] the implementation of a MOS sensor in a microfluidic channel coated with metallic and polymeric layers enhances the selectivity of the sensor to a specific target gas (or gas mixtures). In this thesis, a microfluidic channel with the cross-sectional dimension of 500 μ m×1mmf the length of 3 cm was designed (see Figure 4-4). The diffusion rate of different gases through the microfluidic channel varies based on the size and shape of the gas molecule: large molecules have a longer diffusion time, and smaller ones diffuse faster. The cross-sectional area as well as the length of the channel are two important factors that affect the diffusion of gases through them. The channel dimension has been optimized in [98] and used here.

Another important factor affecting the gas diffusion process through the microfluidic channel is the channel coating. The microfluidic channel is coated with three different metallic and polymeric layers (see Figure 4-5): the channel is first sputtered with a layer of chromium (35 nm thickness). The second layer of sputtering is 65 nm of gold. Finally, a 4-µm layer of Parylene C is coated on top of the other layers using physical deposition using a Parylene C coater machine (SCS-PDS 2010 Labcoater). The aforementioned order of coating layers has shown the best selectivity towards alcohols, ketones, and alkanes [98].

The chromium layer increases the adhesion between the gold layer and the 3D printed microchannel. Gold is one of the most non-reactive materials in nature and increases significantly the recovery time of the sensor. The Parylene C layer acts as a humidity barrier by increasing the surface adsorption of the channel walls to water molecules. Humidity can affect the gas sensing process drastically and results in signals with lower or higher magnitude that changes the results of high precision gas sensing tests. Depending on the analyte type, the combination and thickness

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of coatings can change the adsorption/desorption characteristics of gases through the microchannel.





Figure 4-4 Different views of the microchannel



Figure 4-5 Coated layers inside the microfluidic channel

The THC that is available for performing the tests is already dissolved in methanol. Therefore, evaluation of the sensor performance against methanol seems to be necessary. Figure 4-6 shows the response of the in-house fabricated MOS sensor against different concentrations of methanol. The microchannel slows down the gas diffusion as well as the recovery of the sensor. The magnitude of the signal is damped (compared to the responses observed in Figure 4-3) due to slower diffusion inside the microchannel. Higher concentrations of methanol lead to a higher response from the sensor. The recovery time for a 10 second exposure time is found to be 100 seconds.

The test results of the commercial sensor against different concentrations of methanol are presented in Figure 4-7. Higher concentrations of methanol results into higher signal magnitudes. The magnitude of the responses obtained from the in-house fabricated sensor is 18% less than those obtained using commercial MOS sensor; however, the response time is faster for the in-house sensor.



Figure 4-6 response of the embedded sensor inside the micro channel to different concentrations of methanol



Figure 4-7 Responses of the commercial sensor inside the microchannel to different concentrations of methanol

The in-house fabricated sensor seems to be more sensitive to the mixture of THC and methanol compared to pure methanol based on the results shown in Figure 4-8. The magnitude of the maximum value of the signal for the mixture is 20% higher than that of pure methanol. This difference is solely attributed to the composition of the analytes that are sensed by the sensing layer. The selectivity of the fabricated sensor towards THC will be investigated later on in Section 4.3. Also the recovery time seems to be fairly fast compared to the commercial sensor. Even though the microchannel has decreased the magnitude of the noise, the presence of this systematic noise is still obvious.



Figure 4-8 response of the embedded sensor inside the micro channel to different concentrations of THC and methanol mixture

Figure 4-9 shows the response of the embedded commercial sensor inside the microchannel to different concentrations of THC/methanol mixture. The magnitude of the produced signal by both the commercial and fabricated sensors are almost equal. However since the commercial sensor is more sensitive towards methanol, the in-house fabricated sensor could be potentially more sensitive towards THC molecules. This could be investigated only if pure THC was available for conducting the tests.



Figure 4-9 Responses of the commercial sensor inside the microchannel to different concentrations of THC/methanol mixture

Figure 4-10 compares the responses of the commercial sensor with those of in-house fabricated sensor for 1000 ppm of methanol. The commercial sensor shows better sensitivity towards methanol; whereas both responses have almost the same magnitude towards the THC/methanol mixture (in Figure 4-11). This change in the difference of the responses is attributed to the analytes that the sensors are exposed to.



Figure 4-10 Comparison between the responses of the commercial and in-house built sensors towards 1000 ppm of methanol



Figure 4-11 Comparison between the responses of the commercial and in-house built sensors towards 1000 ppm of methanol/ THC mixture

4.3 Feature extraction model

The feature extraction model uses the common features from the response profile of analytes to segregate them in a feature space. Patterns that are used in this model are the maximum response value (F1), the final readout value (F2) and the area underneath the curve (F3). The latter changes this feature extraction model to phase space integral model [99]. The maximum response value represents the concentration level of the target gas. The last readout of the sensor (the voltage at t = 200 s) which is also close to the baseline, represents the conductance of the sensor when it is chemically stable. Finally, the area underneath the curve represents the average conductance of the sensor when it espects when the analyte is absorbed to the sensing layer. Figure 4-12 shows the three features representation on 2D response curve.

The goal of using this model is to segregate different concentration profiles of THC and methanol in a 3D space. The results of the tests with methanol and mixture of THC/methanol for different concentrations are the inputs to this model. The output will be a point in a 3D space associated with a particular concentration of the analytes. Different responses associated with an analyte can overlap in a 3D space only if common features corresponding to different concentrations are recognized and used.

Figure 4-13 and Figure 4-14 show the features in two separate 2D graphs for the in-house fabricated and commercial sensors, respectively. The role of the feature extraction model is to find common patterns between different concentrations of the same analyte. The model seems to be successful in pattern recognition of the data that is produced by the in-house fabricated sensor (see the clusters of the results of methanol versus the THC/methanol mixture). However, the results of the commercial sensor does not lead to segregation of responses for different analytes. In other

words, the feature extraction model cannot recognize common patterns to segregate different batches of analytes with variable concentrations for the commercial sensor.

Overall, the comparison of the feature extraction model results shows that the in-house fabricated sensor is more selective towards THC molecules compared to the commercial sensor. Even though the magnitude of the response of both sensors towards the mixture of THC/ methanol is similar, the features in the response obtained from the in-house fabricated sensor can be better segregated for THC and methanol data.



Figure 4-12 features that are used for the feature extraction model



Figure 4-13 2D demonstration of the features (F1: maximum response value, F2: final readout value and F3: area underneath the curve) for the in-house fabricated sensor against different concentrations of methanol and mixture of THC/methanol. The points associated with different concentrations of each analyte are successfully segregated in both 2D spaces.



Figure 4-14 2D demonstration of the features for the commercial sensor tested against different concentrations of methanol and mixture of THC/methanol. The model is not able to segregate the data associated with different concentrations of each analyte in this space.

To quantify the segregation of the features, the Mahalanobis distance is calculated. Basically during the tests the same phenomenon is measured by two similar systems. The data that is produced by each sensor is naturally scattered and needs to be normalized. The standard deviation of each set of data can be used for normalization. Using the Mahalanobis distances, the distribution of the data for each test is analyzed. This analysis shows the standard deviation of each point from the center point of distribution in the 2D feature space. The formula to calculate the Mahalanobis distance for 2D space is shown below:

$$d_m(x,y) = \sum_{i=1}^n \sqrt{\frac{(x_i - \bar{x})^2}{\sigma_1^2} + \frac{(y_i - \bar{y})^2}{\sigma_2^2}}$$
(4.1)

In the first step of this analysis, the center point of each distribution in the 2D vector space is obtained. The center points are the average values of each feature (see Table 4.1). Then, the data will be normalized by the standard deviation (listed in Table 4.1) to eliminate the quantitative effect of random distribution.

Sensor & VOC	Parameter	F1	F2	F3
Fabricated sensor	Average	0.0124	0.021	0.0406
Methanol	Standard deviation	0.002074	0.001581	0.007092
Fabricated sensor	Average	0.019	0.0288	0.0812
THC + Methanol	Standard deviation	0.001581	0.001924	0.004919
Commercial sensor	Average	0.0164	0.024	0.0534
Methanol	Standard deviation	0.003578	0.004183	0.014673
Commercial sensor	Average	0.0164	0.024	0.0534
THC + Methanol	Standard deviation	0.003578	0.004183	0.014673

Table 4-1 Average and standard deviation of the data associated with each sensor and target gas

These values of Mahalanobis distances are listed in Tables 4.2 and 4.3. These values show how scattered the data distribution is after normalization. The smaller values for Mahalanobis distances show that the test results of the fabricated sensor inside the microchannel can be segregated based on the target gas in separate zones without any overlap.

Table 4-2 Values of Mahalanobis distance for each 2D feature space for fabricated sensor. Each number shows the cumulative distances of points in 2D feature space from the center of each distribution.

F1 & F2	Methanol	3.96
F1 & F2	THC + Methanol	3.35
F1 & F3	Methanol	2.92
F1 & F3	THC + Methanol	4.21

Table 4-3 Values of Mahalanobis distance for each 2D feature space for fabricated sensor. Each number shows the cumulative distances of points in 2D feature space from the center of each distribution.

F1 & F2	Methanol	12.16
F1 & F2	THC + Methanol	13.12
F1 & F3	Methanol	17.90
F1 & F3	THC + Methanol	15.55

Sensitivity analysis of the fabricated and commercial sensor is shown in Figure 4-15. This graph shows the sensor output voltage as a function of the target gas concentration. The voltage – concentration graph is linear for both commercial and fabricated sensors. For each concentration, tests have been repeated 5 times to ensure reproducibility. Figure 4-16 shows the variation in the

response of the in-house fabricated sensor against the 1000-ppm methanol sample. The changes in the magnitude of the response over different iterations seems to be negligible.



Figure 4-15 Sensitivity analysis of the fabricated and commercial sensor to different VOCs



Figure 4-16 Variations in the sensor responses for five iterations towards 1000 ppm of methanol

Chapter 5: Conclusions and future work

5.1 Conclusion

In this study, a SnO₂-based MOS sensor was fabricated using the electrospinning method. Unlike the commercial sensors embedded in housing, the proposed design does not block the diffusion path of target gases and can be embedded in various high precision gas detectors available in different sizes. The composite Au-doped SnO₂ nanofibers were obtained by sputtering gold, resulting in a more chemically-stable sensing layer. The performance of the sensor fabricated inhouse was compared with a commercial sensor. Also, both sensors were embedded inside a microchannel (used to enhance selectivity of the sensors) and tested against different concentrations of methanol and mixture of THC/methanol mixture. The results show that the inhouse fabricated sensors outperforms the commercial one in terms of the segregated data presented in a 3D feature space. A summary of achievements that were obtained during this study is listed below:

- Two methods of fabrication of metal oxide semiconductors (MOS) including electrospinning and thin file deposition were tested here. The results show that the former produces sensors with much higher sensitivity as compared to the latter.
- A electrospinning deposition setup was built in house. The setup was equipped with in safety cage to minimize any chances of mishap that may occur during the usage of the high voltage power source.
- Pure and composite SnO₂ nanofibers were obtained and calcinated at high temperatures (and characterized through SEM images). The performance of the sensor against different

concentrations of VOCs was investigated. Subsequently, the effect of the calcination temperature and the thickness of the Au doping on the performance of the sensor was studied. As observed from the results, the large surface area to volume ratio of the nanofibers calcinated at 350°C for 4 hours is the main reason for the significant increase in the sensor sensitivity towards methanol and THC molecules. Furthermore, the effect of gold doping on electron absorptivity of the sensing pallet was studied and shown that it improves sensitivity. It was shown that calcination at 350°C and gold-doping of 10 nm produce the highest sensor performance.

- The uniform cyclic response to different concentrations of VOCs and also results of sensor testing across different days, show reproducibility of the sensors for different exposure periods. Reproducibility is attributed to the chemical state of the sensing layer. It was found that the warm-up phase affects the chemical stability of the sensing layer and correspondingly shifts the baseline and magnitude of the response.
- Integrating the sensor into a microchannel (coated with different metallic and polymeric layers) increases selectivity of the sensor towards THC and methanol and mitigates the effects of humidity. The unique combination of coatings inside the channel is the main reason for the enhanced selectivity.
- The results of the feature extraction model show a successful separation of THC from methanol for the in-house built sensor, whereas this was not possible with the commercial sensor. The features that were used for this purpose were maximum value of the response, the area under the curve, and the response value at 200 s. The sensor and microchannel dimension can be modified to fit inside gas detectors with different sizes.

5.2 Challenges and limitations

Most of the challenges that were observed while conducting this study were related to technical aspects. Material selection for the microfabrication process was found to be really challenging. One of the limitations that affected the microfabrication process was the minimum feature (gap) that was possible to apply on the interdigitated electrodes. Based on the technical capacity of the cleanroom facility, this minimum feature is $10 \,\mu$ m. However, when the masks with the $10 \,\mu$ m gap were used, the failure rate was about 50%. In order to resolve this issue the minimum feature was increased to $20 \,\mu$ m to avoid the connection between IDEs. Cutting the silicon wafer substrate was another challenge that affected the project timeline significantly.

Observation of systematic noise in all the readings found to be really surprising at the beginning. Although the signal to noise ratio is less than 5% in all of the graphs presented in this study, knowing the sources of the noise and reducing it was important to improve the performance of the sensor. It was speculated that the main source of this systematic noise is the reduction and oxidization reactions that happen at the same time inside the sensing pallet. The presence of the systematic noise was a challenge that affected the results in addition to other sources of error mentioned below.

Performing standard tests with the same environmental conditions is always difficult since our ability to control atmospheric parameters is limited. To keep consistency during the tests, the number of atmospheric parameters that are monitored should be maximized. These parameters include, but are not limited to, humidity, temperature, pressure and the composition of VOCs in the room.

5.3 Future work

To improve the fabrication process as well as the performance of the fabricated sensor, the following suggestions are presented:

- A temperature study can be performed on the micro-heater to find the optimum operating temperature of the sensor that results in the maximum sensitivity. Additionally, numerical modeling can be performed to simulate the micro-heater performance and find a correlation between the current and temperature of the micro-heater.
- A series of longevity tests can be carried out in order to find the life cycle of the sensor.
 These longevity tests can be performed with different VOCs in order to investigate the effect of each analyte on the life cycle of the sensing layer.
- A wide range of metal nano particles can be added to the sensing layer to form a composite structure for improving the sensitivity of the sensor towards THC. These dopant metals include but are not limited to copper, platinum, iron, zinc, chromium and iridium.
- A conductive polymer can substitute the doping metal and simultaneously the precursor polymer. These conductive polymers must be soluble in the solvents that are used for the electrospinning process.
- Miniaturization of the sensor is an important factor that always leads into more sensitivity.
 Decreasing the substrate size and subsequently the minimum gap between IDEs are two major steps that can lead to miniaturization.

- The effect of the microchannel on the noise control can be studied precisely. Changing the diffusion pattern of the target gases can change the reduction and oxidization reactions significantly.
- The connections made for the sensor and the heater are fairly sensitive and any small movement of the sensor can damage the connections. Using the wire bonding method instead of handmade silver paste connections can be a promising technique to resolve the connection problems.

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