Sensor Array Devices Utilizing Nano-structured Metal-oxides for Hazardous Gas Detection

DISSERTATION

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Abstract

Methane and carbon monoxide are two hazardous gases which require continuous monitoring by gas sensors in underground coal mines for explosion prevention and toxicity, respectively. This work explored implementing miniaturized gas sensors in this area to simultaneously detect both gases for benefits of increased portability and reduced power consumption of the chemiresistive gas sensor device. The focus of this research was to understand how the particle size, morphology, and microstructure of the metal-oxide film affected the gas sensor performance to the two gases of interest on miniaturized gas sensor devices in the form of microhotplate platforms. This was done through three main research studies.

The first was conducted by growing SnO$_2$ nanowires from SnO$_2$ particles using an Au-catalyst. Growth conditions including temperature, time, and oxygen partial pressure were explored to determine the formation aspects of the SnO$_2$ nanowires. Gas sensor studies were completed that provided evidence that the SnO$_2$ nanowires increased detection to a fixed concentration of carbon monoxide compared to SnO$_2$ particles without nano-structure formation.

A second research study was performed to compare the gas sensor performance of SnO$_2$ nanoparticles, hierarchical particles, and micron-size particles. The nanoparticles were developed into an ink and deposited via ink-jet printing on the microhotplate substrates to control the microstructure of the metal-oxide film. By preventing
agglomeration of the nanoparticle film, the SnO$_2$ nanoparticles displayed similar gas sensor performance to methane and carbon monoxide as the hierarchical particles. Both nano-structures had much higher gas sensor response than the micron-size particles which confirms the surface area of the metal-oxide film is critical for reaction of the analyte gas at the surface.

The last research study presented in the dissertation describes an oxide nanoparticle array developed for detecting methane and carbon monoxide in the presence of one another. A design of experiments was constructed and principal component analysis was used for determining the optimum temperatures of the metal-oxide elements. A four element array was developed with the SnO$_2$ and TiO$_2$ sensor elements able to detect methane concentrations of interest and the ZnO and NiO sensor elements able to detect the carbon monoxide concentrations. A linear based prediction model was developed and tested for accuracy and reproducibility of the model to a series of random gas concentrations.
Dedication

This document is dedicated to Beth and my family.
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I would like to thank my thesis adviser, Dr. Patricia Morris, for giving me the opportunity to work on a challenging and exciting project during my graduate studies. She gave me the freedom to think independently and grow personally, and she also challenged me to explore difficult subjects and manage students which will be invaluable throughout my career. I would also like to thank, Dr. Sheikh Akbar, for helpful discussions on gas sensor technology.

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To my fiancé, Beth, your understanding and support during my graduate studies have been tremendous. Seeing your ambition for your career has shown me how much strength and courage you have, and to always pursue our dreams and goals.
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Chapter 1: Introduction

Gas sensor technology is a vast scientific area of research that focuses on detecting gas molecules in the environment for numerous applications. There are several kinds of gas sensors that have been developed based on different sensing materials with unique sensor geometries and various transduction platforms. The main classes of gas-sensing materials include metal-oxide semiconductors, intrinsically conducting polymers, conducting polymer composites, metal-oxide/polymer composites, and other novel materials [1]. These materials can be applied on different sensor platforms including chemiresistive, metal-oxide semiconductor field-effect transistor (MOSFET), quartz crystal microbalance, optical transducers, and surface acoustic wave. In addition, other gas detection methods include hybrid fiber optic methods [2], gas chromatography mass spectrometry (GC-MS), and fourier transform infrared radiation (FTIR). Among these techniques, gas sensors based on chemiresistive semiconducting metal-oxides have many potential benefits including, but not limited to, their very low cost, high sensitivity, fast response/recovery time, simple electronic interface, ease of use, and ability to detect a large number of gases [3]. While there are numerous types of solid-state gas sensors, only chemiresistive gas sensors based on semiconducting metal-oxides will be discussed as part of this document. Some examples of metal-oxides that are used for these gas
sensors are wide-band gap semiconductors which include SnO₂, WO₃, In₂O₃, ZnO, TiO₂, Fe₂O₃, Co₃O₄, and NiO [4].

Since the pioneering work by Taguchi and Seiyama et al. in 1962, chemiresistive gas sensor devices based on semiconducting metal-oxides have been used to monitor various gases for several applications relating to environmental monitoring [5, 6], odors [7], hydrogen sensing [8, 9], and liquefied petroleum [10]. In addition, stricter regulations are being put in place on the emissions of hazardous gases from automobiles such as carbon monoxide (CO), hydrocarbons, NOx (NO and NO₂), ammonia [11, 12], and in cabin monitoring [13]. Other important fields for gas sensor technology include homeland security for the detection of chemical warfare agents [14], food industries to analyze the complex gases evolved from food ageing and spoilage [15-17], and the medical sector which is interested in the detection of specific gases related to diagnostics and patient monitoring [18, 19]. One of the more recent trends in gas sensor technology is the development of an “electronic nose” which has been extensively discussed in the medical field for applications such as non-invasive diabetes monitoring [20] and conditions related to expelled gases in the human breath [21]. These solid-state gas sensors are also called chemiresistors due to the change in electrical resistance when reducing or oxidizing gases are present.

The primary goal of this research is to create a chemiresistive gas sensor array based on nano-structured metal-oxides on a miniaturized platform to detect methane and carbon monoxide for improvements to coal mine safety. In order to achieve this goal, several important studies were completed. This introduction will be used to provide the reader
with a description of the detection limits that are required of the chemiresistive gas sensor for the application of this research and the challenges of utilizing a miniaturized sensing platform. These descriptions are necessary to explain why certain experimental methods and techniques were used for this research project. The succeeding structure of this dissertation will be as follows. Chapter 2 will provide an explanation of the working principles of chemiresistive metal-oxide sensors including adsorption of oxygen ions on the surface, reaction with reducing/oxidizing gases, and definitions for gas sensor response and selectivity. This chapter will also outline the relationship between particle size and gas response and describe the recent focus of gas sensor research on synthesizing and implementing nano-structured metal-oxides as the sensing layer for the device.

Chapter 3 will investigate the growth of SnO₂ nanowires from SnO₂ particles using an Au-catalyst. Gold nanoparticles were coated on the SnO₂ particles using a wet chemistry technique and optimal growth conditions (temperature, time, oxygen partial pressure) were explored. This nano-structure was subjected to gas sensor testing to carbon monoxide to compare the performance of SnO₂ films before and after SnO₂ nanowire formation. Chapter 4 focuses on nanoparticle and nano-structure synthesis using hydrothermal and solvothermal techniques, ink formulation, and the subsequent deposition of these materials on microhotplate platforms via an ink-jet printer or picopump. For compatibility with the ink-jet printer, there are several critical rheological properties that must be controlled to form drops to produce the metal-oxide film on the miniaturized substrates. These rheological properties are examined as well as the printing profile needed for coverage of the microhotplates.
Chapter 5 compares the gas sensor performance of SnO$_2$ nanoparticles, nanostructures, and micron-size particles on microhotplate platforms to methane and carbon monoxide gas. This study was done to explore the impact of particle size, surface area, and microstructure of the metal-oxide film on gas sensor performance. Chapter 6 concludes the dissertation through the development of a gas sensor array using metal-oxide nanoparticles to detect methane and carbon monoxide for coal mining applications. A design of experiments (DOE) matrix was constructed and principal component analysis was used to determine the optimum temperature for each material to selectively detect methane or carbon monoxide in the presence of the other gas. A linear based prediction model was created for the sensor array with the metal-oxide resistances corresponding to the analyte gas concentrations. This model was tested for accuracy through validation testing to several carbon monoxide and methane concentrations.

1.1 Detecting Hazardous Gases for Coal Mining Applications

As stated previously, there are numerous applications for chemiresistive metal-oxide gas sensors in air quality control. The Orton Ceramic Foundation provided funding for the research disclosed in this dissertation and through their collaboration; we determined the application for this research would focus on developing gas sensors for detecting methane and carbon monoxide for coal mining applications. The following section gives a brief description of the history and current technology used in sensing these analyte gases.
A division of the Center for Disease Control (CDC), the National Institute for Occupational Safety and Health (NIOSH) has established guidelines for methane and carbon monoxide levels in coal mines. The NIOSH Office of Mine Safety and Health Research has established a Ventilation and Explosion Prevention Program to improve mine air quality and reduce explosion hazards by developing and implementing advanced scientific ventilation technologies and practices [22].

Recent explosions in underground coal mines resulted in 65 fatalities and 18 injuries in the past 10 years [22]. This includes the Sago Mine in West Virginia (12 fatalities) and the Darby No. 1 Mine in Kentucky (5 fatalities) in 2006 and the Upper Big Branch Mine in West Virginia (29 fatalities) in 2010. The Mine Safety and Health Administration (MSHA) which is part of the U.S. Department of Labor is the federal enforcement agency responsible for investigating and documenting incidents at coal mines. A recommendation of the MSHA following the Sago Mine explosion was to make more frequent tests for methane gas during winter months. MSHA dictates that hazardous gas detection is one of the best practices to prevent explosions in underground coal mines. This includes atmospheric monitoring systems to monitor strategic locations for carbon monoxide, oxygen content, and methane content as well as frequent checks of methane and oxygen levels especially during periods of rapid decline in barometric pressure [23]. The concentrations of methane and carbon monoxide that are of importance for the application of monitoring in coal mines are described below.
1.1.1 Methane

The MSHA has established exposure limits for methane in coal mines to ensure the safety of underground coal mine workers. The Federal Coal Mine Health and Safety Act of 1969 established the exposure limit to be one percent of methane (CH$_4$) by volume for coal miners to operate in underground mines [24]. At a two percent concentration of methane, power must be removed from the mining equipment and the entire mining process must stop [25]. Methane is most explosive in air at higher concentrations (5 to 15% in air), but federal regulations mandate lower levels and require methane sensors on certain mining equipment. Explosions can be prevented or mitigated by eliminating ignition sources and by minimizing methane concentrations.

While not currently mandated, it is necessary for mine personnel to be provided with methane monitors that can be worn while working in areas that cannot be regularly monitored. The other option is to have remote methane detectors located throughout the underground mine. Challenges lie in this implementation because as the “face” of the mine continuously moves, it would be time consuming and not cost effective to continuously move the location of the methane sensors. It would be more beneficial to have them remotely located on personnel and equipment.

Methane sensors in the form of methanometers are currently used to satisfy the MSHA requirement. Methanometers are selective methane sensors which operate as a catalytic heat of combustion sensor with a very fine platinum wire contained within an alumina bead coated with a catalyst material [24]. During operation, the active bead is heated to a temperature sufficient to promote combustion of the methane gas with oxygen
on the surface of the catalyst. The increased heat generated by the combustion increases
the resistance of the wire on the inside and this corresponds to the concentration of
methane in the atmosphere. The methanometer must come with dust cap and flame
arrester to prevent flame outside of device and the dust cap negatively impacts response
and recovery time of the device. The methanometers are required to be calibrated every
31 days and predicted methane concentrations must be within 0.2% of actual calibration
gas.

### 1.1.2 Carbon Monoxide

Carbon monoxide (CO) is a toxic, odorless gas that is present in many underground
mines. Adverse health effects from carbon monoxide are due to the formation of
carboxyhemoglobin in the blood, which inhibits oxygen uptake. According to NIOSH,
the exposure limit for a healthy worker over an eight hour day is 35 ppm while 1,200
ppm of carbon monoxide is Immediately Dangerous to Life and Health (IDLH). A table
describing the effects of increasing carbon monoxide concentrations on the human body
is shown in Table 1.1.
Table 1.1: Effects of carbon monoxide on the human body (image from Ahlborn [26]).

The ambient concentrations in coal mines in Pennsylvania and West Virginia are 0 to 4 ppm CO and for some coal mines in Illinois and Colorado are 12 ppm carbon monoxide. Monitors regulated by the MSHA require alarms for CO concentrations greater than 10 to 15 ppm above the ambient level of the mine [2]. This would put the allowable carbon monoxide limit between 10 and 30 ppm. Currently, there are electrochemical sensors used to detect carbon monoxide in coal mines which uses a cell with an ion-exchange membrane solid electrolyte with a three-electrode structure (working, counter, and reference electrodes) [2]. These electrochemical sensors are only selective to carbon monoxide and cannot detect methane. Recently there has been research for hybrid fiber-optic electrochemical selective carbon monoxide sensors as well [26].

By federal law, these two hazardous gases require continuous monitoring in coal mines. Currently, two separate sensors are used to detect methane and carbon monoxide
at the concentrations of interest. This research project involves implementing semiconducting metal-oxide gas sensors using array technology to monitor both methane and carbon monoxide simultaneously with one device. This is viable since metal-oxides respond to several reducing and oxidizing gases including methane and carbon monoxide, and metal-oxides are sensitive at these analyte concentrations. Another capability of the chemiresistive gas sensors is the sensor geometry can be manufactured to be very small. Portability and low power consumption are important characteristics needed for this application as well, and a discussion of the sensor substrates is given in the next section.

1.2 Implementing Miniaturized Sensors

There are numerous configurations for chemiresistive gas sensor devices, but all are composed of four essential parts. The sensing material (metal-oxide particles) are generally deposited as a polycrystalline film or porous layer on a ceramic substrate with integrated noble metal electrodes (e.g. gold, platinum) for resistance measurements. The sensor also typically comes with a heating element for operation at elevated temperatures [27]. Chemiresistive metal-oxide gas sensors operate at elevated temperatures (200-600°C), and this temperature depends on the material, adsorbed oxygen species on the surface, and analyte gas of interest. This will be developed in more detail in Chapter 2. A schematic of one type of sensor platform for chemiresistive gas sensor devices is shown in Figure 1.1 [28].
Figure 1.1: Diagram of commercial gas sensor platform with alumina substrate, interdigitated electrodes, heater, and a metal oxide layer (image from Moulson [28]).

The diagram in Figure 1.1 depicts a microporous SnO$_2$ layer on top of an alumina substrate with interdigitated sensing leads and an integrated heater on the bottom of the substrate. The size of the chemiresistive sensor substrate is important for two main reasons when determining feasibility in commercial applications. The first is the physical size of the device for portability and access to the regions of interest during gas sensing. The second is the power consumption associated with heating the sensor platform to the desired temperature for gas sensing. The substrate is typically made from alumina which has a very low thermal conductivity. It takes a significant amount of energy to heat the alumina to the desired temperature. Additionally, the larger the substrate, the more energy required to heat the device. A diagram of a traditional alumina substrate for thick-film metal-oxides that is commercially available from Case Western Reserve University is shown in Figure 1.2.
The dimensions of the alumina sensor substrate are 15x15 mm with the electrodes occupying a 10 mm x 10 mm area. This specific sensor substrate does not include an integrated heater, but for experimental practices an external heater in the form of a tube furnace was utilized. The alumina sensor substrate is only one type of sensor platform as there has been recent developments in sensor technology to implement miniaturized sensors. These miniaturized sensors have silicon platforms with dimensions in the micron range. These low power devices are called microhotplates, and research groups have found them to be beneficial for future gas sensor technology as device miniaturization continues [29-31]. In Figure 1.3, a size comparison is given between the alumina sensor substrate in Figure 1.2 (A), a singular microhotplate (B), and a 4x4 microhotplate array (C).
Figure 1.3: Photograph of several metal-oxide gas sensor substrates for a size comparison next to a dime: (A) alumina sensor substrate, (B) microhotplate platform from Kebaili Corporation, and (C) 4x4 microhotplate array from NIST.

The alumina sensor substrate in (A) from Figure 1.3 was described previously and physically has dimensions similar to that of a U.S. dime. The singular microhotplate designated by (B) in Figure 1.3 is a singular microhotplate. The microhotplate is a sensor substrate manufactured by the Kebaili Corporation which includes gold electrodes, an insulating SiO$_2$ layer, a platinum heater, and a silicon nitride base. The dimensions of the microhotplate are shown in Figure 1.4.
From Figure 1.4, it can be seen that the distance between the electrodes is 250 microns for the microhotplate from the Kebaili Corporation. This is approximately a 50x decrease in area compared to the traditional alumina sensor substrate from Case Western Reserve University. These are the only commercially available microhotplate substrates for gas sensor measurements the author was able to locate and purchase. For chemiresistive metal-oxide sensors, it is necessary to use multiple metal-oxides and/or operating temperatures to construct an array for gas discrimination. While the singular
microhotplate from Kebaili can only consist of one sensor material, technology exists at the National Institute of Standards and Technology (NIST) in the form of microhotplate arrays. A 4x4 microhotplate array is shown in (C) in Figure 1.2 which consists of 16 individual sensor elements. A magnified image of the microhotplate array from NIST is shown in Figure 1.5.

**Figure 1.5**: Optical image of microhotplate 4x4 array from the National Institute of Standards and Technology (NIST).

The microhotplate array from NIST is fabricated differently than the microhotplate from Kebaili, but they both use silicon processing techniques, incorporate an integrated
heater with a controllable heater, and have electrodes for recording resistances of the metal-oxide films when exposed to analyte gases. The NIST microhotplates have platinum interdigitated electrodes and a polysilicon heater which differs from the Kebaili microhotplate. However, both microhotplate devices are physically small and consist of small areas for which the metal-oxide films need to be heated. This corresponds to good portability and low power consumption which is beneficial for our application in coal mines.

The microhotplate arrays from NIST are not commercially available, so the microhotplates from Kebaili were primarily used in this gas sensor research. There are inherent difficulties with producing a metal-oxide film on sensor substrates in the form of microhotplates due to the physical size of the platform. This will be discussed at length in Chapter 4, but this introduction was designed to illustrate the benefits of using miniaturized sensor substrates. Now that the chemiresistive sensor substrates and analyte gases of interest for this research project have been defined, Chapter 2 will focus on nano-structured metal-oxides and the microstructure of the metal-oxide film that result after depositing these materials. This is critical to the operation of the device as the metal-oxide particles serve as the sensing element for the gas sensors.
Chapter 2: Chemiresistive Gas Sensor Technology

The working principles of chemiresistive sensors are necessary to understand for the subsequent chapters in this dissertation. While there are numerous review articles describing the operation of metal-oxide sensors, the objective of this section is to introduce and describe two important properties of the metal-oxide sensing layer critical for device performance [3, 5, 32-36]. The first is the effect of metal-oxide particle size and particle morphology on the sensing properties. Particle morphology describes the size and shape of the metal-oxide particles, and definitions for nanoparticles and nanostructures will be outlined. The second main topic will describe the metal-oxide film microstructure, and how the porosity influences the resistance change in the material during device operation especially for nanoparticulate films.

It is important to note that there are two main types of semiconducting metal-oxides used in chemiresistive sensors. The first type is n-type semiconductors whose majority carriers are electrons, and this includes SnO₂, TiO₂, ZnO. The other type of metal-oxides used is p-type semiconductors whose majority carriers are holes (NiO, Co₃O₄). The majority of semiconducting metal-oxides used in chemiresistive sensors are n-type because electrons are naturally produced via oxygen vacancies at the operating temperature of the sensors. However, p-type metal-oxides can be very useful in array technology for signal processing.
2.1 Working Principles of Gas Sensors

The fundamentals of a semiconducting gas sensor using metal-oxide particles will be discussed in this section. This is broken down into three processes which provide a solid background for understanding the overall operation of a gas sensor device. The first section describes the adsorption of oxygen on the surface of the metal-oxide and the corresponding band bending that occurs at the surface. The second process is the detection of an analyte gas by a reaction with the adsorbed oxygen and subsequent electronic change at the metal-oxide surface. The last section will describe how the electron transfer at the surface of the metal-oxide particle leads to a change in the overall resistance of the metal-oxide film.

2.1.1 Adsorption at Surface and Band Bending

It is energetically favorable for oxygen, which makes up 20.8 volume percent of air, to adsorb on the surface of metal-oxide particles [37]. Adsorption of oxygen on the metal-oxide surface can take place in the form of physisorption or chemisorption [33]. Physisorption is a weak adsorption process that generally develops from a dipole-dipole interaction between gas molecules and a material’s surface. In physisorption, there is no change in the electronic structure of the metal-oxide surface. The other adsorption event that can take place is chemisorption which is the chemical reaction of oxygen at the metal-oxide surface which involves the transfer of electronic charge [33, 38]. These adsorption events depend on the temperature and partial pressure of oxygen in the
environment [39]. For temperature ranges necessary for chemiresistive metal-oxide gas sensor operation, oxygen is ionosorbed on the metal-oxide surface. In ionosorption, oxygen acts as a surface state, capturing an electron or hole depending on the type of semiconductor (n-type or p-type) [33]. The charged oxygen is bound to the metal-oxide surface by electrostatic attraction. In n-type semiconductors, ionosorbed oxygen atoms act as surface acceptors by binding electrons which leads to a decrease in the surface conductance of the material [34].

Oxygen can be ionosorbed onto the metal-oxide surface in several forms [28]. At lower temperatures (150-200°C), oxygen does not dissociate and adsorbs in a molecular form as either neutral O₂ or charged O₂⁻. At temperatures greater than 200°C, oxygen dissociates and adsorbs as O⁻ ions [39]. In addition to O⁻ ions, adsorbed O²⁻ ions can also form at temperatures above 400°C. Chemiresistive sensors are generally operated above 300°C in order to enhance the reaction kinetics for reducing gases to react with the ionosorbed oxygen at the surface [5].

The electrons that are extracted from the metal-oxide surface originate from donor sites in the material [7]. These donor sites generally come from intrinsic oxygen vacancies that are extracted from the conduction band of the material and become trapped at the surface. As the adsorption proceeds, a space-charge layer develops as electrons transfer from donor defects to the ionosorbed oxygen [28]. As numerous adsorption events occur on the surface of the metal-oxide, there is a build-up of charge on the surface. The electron transfer from the bulk of the material to states at the surface of the metal-oxide leads to upward band bending for an n-type semiconductor [40].
bending produces a surface potential barrier denoted by $eV_{\text{surface}}$ which has an energy between 0.5 to 1 eV. A schematic showing the band bending that occurs when oxygen ions adsorb to the surface of an n-type semiconductor is shown in Figure 2.1 [7].

![Figure 2.1](image)

**Figure 2.1**: Schematic showing band bending in n-type semiconductor with O$^-$ adsorbed on surface sites. Valence band ($E_V$), conduction band ($E_C$), and Fermi energy ($E_F$) are denoted. Width of space-charge layer ($\Lambda_{\text{air}}$), electrons ($e^-$), and donor sites (+) are also shown (image from Franke [7]).

The diagram in Figure 2.1 shows the band structure for a wide band-gap n-type semiconductor with the conduction band ($E_C$), valence band ($E_V$), and Fermi energy ($E_F$) clearly displayed. An oxygen molecule in the gas phase ($O_2, \text{gas}$) approaches the surface,
dissociates, and extracts an electron to form a chemisorbed oxygen ion on the surface (O\textsuperscript{−}\textsubscript{surface}). The donor sites are designated by the + sign in Figure 2.1 and the width of the space-charge layer is shown by Λ\textsubscript{air}. The value (height of eV\textsubscript{surface}) of the surface potential and width of the depletion region (Λ\textsubscript{air}) are determined by the quantity and type of adsorbed oxygen on the surface [28].

This width of the space-charge layer is different for each metal oxide and depends on the specific donor concentration as well as the Debye length of the material [41]. This is important for selectivity between gases and is at the forefront of gas sensor array technology. The Debye length, L\textsubscript{D}, is given by equation 2.1.

\begin{equation}
L\textsubscript{D} = \sqrt{\frac{\varepsilon_0 k_B T}{q^2 n_d}}
\end{equation}

In this equation, ε\textsubscript{0} is the permittivity of free space, ε is the dielectric constant, k\textsubscript{B} is Boltzmann’s constant, T is the operating temperature, q is the electron charge, and n\textsubscript{d} is the carrier concentration. The carrier concentration is equivalent to the donor concentration assuming full ionization. As an example, the Debye length of SnO\textsubscript{2} at 250°C and for n\textsubscript{d}=3.6x10\textsuperscript{24} m\textsuperscript{−3}, L\textsubscript{D}=3 nm [7]. The Debye length of the material is generally used to as an estimate for the width of space-charge layer for metal-oxides used in gas sensor technology [42]. This will be further discussed in the section regarding particle size effects in gas sensing.
Now that the details of the surface of the metal-oxide have been described, the reaction of a reducing or oxidizing gas with the oxygen ions on the surface can be developed. Metal-oxides are used to detect numerous gases including O₂, CO, NH₃, NO₂, H₂S, H₂, and C₂H₅OH among others [43, 44]. The mechanism of carbon monoxide, CO, detection for an n-type semiconductor can be summarized in using the following equations [44]:

**Step 1:**

\[
O₂ \text{ (gas)} = O₂ \text{ (adsorbed)}
\]

\[
O₂ \text{ (adsorbed)} + e^- = O₂^-
\]

\[
O₂^- + e^- = 2O^-
\]

**Step 2:**

\[
CO\text{ (gas)} + O^- = CO₂ + e^-
\]

In the first step, the surface of the sensor material is covered with chemisorbed oxygen ions as described previously. An oxygen molecule dissociates and forms two ionized oxygen atoms (2O⁻). The second step is a detecting reaction. In this step, a reducing gas such as carbon monoxide reacts with ionosorbed oxygen on the surface of the metal-oxide. A schematic of this process is shown in Figure 2.2.
Figure 2.2: Schematic of reaction of carbon monoxide (CO) at surface of n-type semiconductor.

The reaction donates a previously surface-bound electron back into the bulk of the material. This leads to a decrease in the space-charge layer and decreases the overall resistance of the metal-oxide. In gas sensor literature, results are sometimes given as a decrease in resistance and alternatively given as an increase in conductance. These are equivalent as $G = \frac{1}{R}$. Electron motion between metal-oxide particles which leads to the overall conductance in gas sensor devices will be discussed in the next section. Conversely, oxidizing gases (such as NO$_2$) immobilize more electrons in the conduction band by creating additional surface-acceptor states [27]. This increases the width of the space-charge layer and causes an increase in the resistance of the material. For p-type semiconductors, such as NiO and Co$_3$O$_4$, reducing gases increase the resistance and oxidizing gases reduce the resistance of the metal-oxide film.
2.1.3 *Electron Motion between Particles*

The sensing layer is generally made up of metal-oxide particles deposited on the substrate in order to create a porous polycrystalline film with adhesion to the electrodes. The electrical conductance occurs through grain-to-grain contacts of adjacent particles. A schematic of a few grains of particles which displays the oxygen adsorption, associated space charge layer, and the band structure is shown in Figure 2.3.

**Figure 2.3**: Schematic of grains of n-type semiconductor with oxygen adsorption and associated band structure (image from Madou [33]).
The space-charge layer, which is depleted of electrons, is more resistive than the bulk of the metal-oxide. Therefore, the contacts between grains provide most of the film resistance. Electrons traveling between particles must overcome the surface potential (in this schematic denoted as $qV_s$) which represents the energy or Schottky barrier between grains [35]. The conductance of the metal-oxide film is given by the equation 2.2.

\[
G = G_0 \exp \left( -\frac{qV_s}{kT} \right)
\]  

(2.2)

In equation 2.2, $G_0$ is the initial conductance in the films. The intergranular contacts are important for the overall performance of the sensor device because the conductance change in the metal-oxide film is associated with the transfer of electrons between these contacts [45].

This is a simplified model of the gas detection and motion of electrons in the sensing film and factors such as film thickness and agglomeration of particles in the film will be discussed in later sections. The principles presented in this section on the interaction of an oxidizing or reducing gas with the oxygen ions on the surface of the metal-oxide have been presented in an ideal way [32]. Other conditions such as humidity in the atmosphere and surface defects will affect the performance of the gas sensor.

2.1.4 Sensor Properties

Upon exposure to a reducing or oxidizing gas (sometimes designated as an analyte gas) of a low concentration in air, the conductance or resistance of the metal-oxide film
will change as described previously. This change in electrical resistance is from a background level typically in air (R_{air}) to a steady level (R_{gas}) on exposure to the analyte gas [5]. When the analyte gas is removed or turned off, the electrical resistance should return to the level in air once again. A typical plot for an n-type semiconductor that is exposed to a fixed concentration of a reducing gas is shown in Figure 2.4.

![Sensor graph showing response to a reducing gas for an n-type metal-oxide](image from Yamazoe [5]).

*Figure 2.4:* Sensor graph showing response to a reducing gas for an n-type metal-oxide (image from Yamazoe [5]).

Two important quantities of the gas sensing material are calculated from a graph such as the one in Figure 2.4. The first is the gas sensor response, sensitivity, of the material to a specific concentration of gas. The sensitivity is reported in a few different forms in gas sensor literature [5, 10, 46], but is generally in some form of the ratio of the resistance when exposed to the analyte gas (R_{gas}) to the resistance in the background (R_{air}).
or \( R_o \). The different forms of sensitivity, \( S \), found in literature are given in equations 2.3 through 2.6.

\[
S = \frac{R_{\text{gas}}}{R_{\text{air}}} \quad \text{(2.3)}
\]

\[
S = \frac{R_{\text{air}}}{R_{\text{gas}}} \quad \text{(2.4)}
\]

\[
S = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \quad \text{(2.5)}
\]

\[
S(\%) = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \times 100 \quad \text{(2.6)}
\]

If a complex background is used instead of a background of air, then \( R_{\text{air}} \) is replaced with \( R_o \) (resistance of metal-oxide in background gas). It is important to understand how the sensitivity is reported for a gas sensor measurement in order to compare and contrast results found in literature. The background concentration of gas will also affect the sensitivity calculation and should be considered as well. Throughout this dissertation, the sensitivity or gas sensor response, will be defined as the ratio: \( \frac{R_{\text{air}}}{R_{\text{gas}}} \). With this convention, for an n-type semiconductor exposed to a reducing gas such as carbon monoxide, the resistance will decrease during analyte gas exposure. Therefore, the gas sensor response will be greater than one. For p-type semiconductors, the gas sensor response will be between 0 and 1. One is defined as the baseline, or no detection of gas,
for chemiresistive metal-oxide sensors since the resistance in the background is equivalent to the resistance during exposure to the analyte gas.

For detecting trace levels of gases it is important to have high sensitivity so the sensing device can show strong and noise-free change in resistance upon the increase or decrease in analyte gas concentration [27]. There are many techniques to improve the performance of metal-oxide gas sensors which consist of doping the metal-oxides [47] and adding metal catalysts to the surface [48]. Metal catalysts serve to increase the reaction kinetics of the analyte gas with oxygen ions which can lead to a greater sensitivity [5]. This will be briefly discussed in Chapter 3, but is not the focus of this literature review on chemiresistive metal-oxide gas sensors.

The temperature of the metal-oxide has been described as critical to the gas sensor operation due to the chemisorbed oxygen ion species on the surface of the metal-oxide. This was also demonstrated through the research of Yamazoe et al. for a SnO₂ gas sensor for the detection of an inflammable gas [5]. The research group found that the sensitivity went through a maximum as shown in Figure 2.5 [5].
From Figure 2.5, it can be seen that the gas sensor response, $\frac{R_{\text{air}}}{R_{\text{gas}}}$, has a maximum between 300-400°C. This is due to the analyte gas type, metal-oxide sensing layer, and oxygen species adsorbed on the surface at these temperatures. Another important sensor property besides gas sensor response is the response and recovery rate of the material. This is important for the quick detection of gases during operation of the device. Response times are generally defined as the time required for the resistance or conductance to attain 90% of its maximum or minimum value [44]. Recovery is defined as the time required for the resistance to return to 10% of its maximum or minimum.
resistance. The response and recovery times are sometimes denoted as $\tau_{\text{resp}}$ and $\tau_{\text{rec}}$, respectively. Both the sensitivity and response and recovery times are very much dependent on the operating temperature.

Generally, the optimum operating temperature is defined as the temperature at which a gas sensor shows maximum sensitivity to a specific analyte gas concentration. However, this is not entirely the case since the sensing performance is characterized not only by sensitivity but also by the response and recovery time as well as selectivity [49]. Thus, a contradiction may develop from the so-called optimum operating temperature. For example, the work of Zhang et al. resulted in a SnO$_2$ hollow sphere sensor with a maximum sensitivity to NO$_2$ at 160°C, but the recovery time was longer at 160°C compared to that at 220°C [49]. Also, the reaction of a specific reducing or oxidizing gas with the ionosorbed oxygen at the metal-oxide surface depends on the temperature. Therefore, different analyte gases have different temperatures that give the highest sensitivity and shortest response and recovery times for the same sensing layer. The importance of operating temperature will also be presented for the influence it has on the diffusion of gas molecules into the porous sensing layer.

In addition to sensitivity and response and recovery times, selectivity is critical for the operation of a gas sensing device. Selectivity is the change in resistance of the material to only one specific gas or a group of gases. Metal-oxides are well known to have selectivity or cross-sensitivity drawbacks especially for automotive applications [11]. For metal-oxide gas sensors, it is difficult to configure the material to detect only one gas. For example, SnO$_2$ will show sensitivity to concentrations of CO, CO$_2$, CH$_3$CH$_2$OH, H$_2$, 

29
H₂O, H₂S, NH₃, NOₓ, O₂, and SO₂ [3]. Instead of attempting to make a highly selective material, gas sensor array devices are used with multiple materials to resolve the issue of selectivity for metal-oxide sensors. Increasing the selectivity (and therefore reducing the cross-sensitivity of the device and can be accomplished through the use of pattern recognition [15, 50, 51]. These techniques utilize multiple n-type and p-type metal-oxides in order to distinguish specific gases in a complex background. An algorithm is used to calculate the species and concentration of gas from multiple resistance measurements using regression analysis.

Metal-oxides used for gas sensors also have drawbacks of long-term stability since they are operated at an elevated temperature to increase the performance in terms of higher sensitivity. At elevated temperatures, metal-oxide particles (especially nanoparticles) may grow in size due to sintering [28]. The driving force for sintering is the reduction in surface energy (curvature) at the interface between particles. A change in the microstructure such as the increase in particle size due to sintering of the metal-oxide film causes a baseline change in the resistance of the material which is also known as drift [52]. Drift is a problem for metal-oxide gas sensor devices because the change in background resistance will affect the sensitivity. Drift is detrimental for sensor devices used in commercial applications where initial calibrations may become invalid.

This description of the working principles for metal-oxide gas sensors was presented in order to have a foundation for the operation of these devices. The importance of controlling the particle size, particle morphology, and film microstructure will be developed in the subsequent sections because these factors greatly influence the
sensitivity as well as the response and recovery times of these devices. Novel techniques that are currently being implemented to tailor metal-oxide particles aim to impact gas sensor technology by being able to detect concentrations in the parts per million (ppm) and parts per billion (ppb) range.

2.2 Particle Size and Film Microstructure Importance for Gas Sensing

The key parameters for the applicability of a sensor include the sensitivity, stability, selectivity, and response and recovery times of the device [3]. Some of the drawbacks of using chemiresistive sensors based on metal-oxides include the lack of stability and reproducibility as well as low sensitivity to trace amounts of gases [33]. In order to increase the sensitivity of the material, controlling the particle size, particle morphology, and microstructure of the sensing layer is of critical importance. Recently, new particle morphologies and deposition techniques have been implemented in order to create a metal-oxide sensing layer with high sensitivity and short response and recovery times for quick detection to small quantities of oxidizing and reducing gases. Sensor characteristics such as sensitivity and response and recovery times have been defined in the previous section for understanding of desired properties during operation. The metal-oxide sensing layer is the most important component of the sensor device that influences these properties. Therefore, the metal-oxide particles that make up the sensing film will be the focus of this discussion.

As described previously, the reaction between reducing or oxidizing gases with the adsorbed oxygen ions on the surface leads to a change in the resistance of the metal-oxide
It has been shown throughout gas sensor literature, that the particle size used in the sensing film greatly influences the sensitivity of the material to a certain concentration of target gas \([5, 7, 35, 41, 53, 54]\). Nanoparticles have shown an increased sensitivity and shorter response and recovery times compared to micron size particles due to larger surface-to-volume ratio \([7]\). Metal-oxide nanoparticles have a much higher surface area compared to micron size particles. This increased surface area allows for more oxygen adsorption on the surface and potential reactions with analyte gases which alters the resistance of the material.

### 2.2.1 Particle Size Importance

In addition to a larger surface-to-volume ratio, reducing the grain size to twice the distance of the space-charge layer of the material has shown to greatly improve the sensitivity \([5]\). From the previous section describing adsorption and band bending at the surface of the metal-oxide, the Debye length of the material is used as an estimate for the width of the space-charge layer. The width of the space-charge layer \((\Lambda_{\text{air}})\) that arises from oxygen adsorption at the surface is essentially kept constant for different particle sizes. It should be noted that the use of grain and particle are often interchanged for one another. The proportion of space-charge layer in each grain, however, will change relative to differences in the particle diameter (sometimes denoted \(d_m\)). A critical particle diameter corresponds to a value that is twice the \(\Lambda_{\text{air}}\). At this critical grain size, the space-charge layers overlap and the particle is considered depleted of electrons \([5]\). The electrical properties for particle sizes less than \(2\Lambda_{\text{air}}\) are dominated by the surface states of the material. The Debye length for SnO\(_2\) at 250\(^\circ\)C was calculated in the previous
section to be 3 nm. Therefore, for SnO\textsubscript{2} particles less than 6 nm in diameter, the depleted particles should lead to an enhanced sensitivity.

Yamazoe et al. performed experiments in order to verify this claim. They monitored the sensitivity as a function of grain size for SnO\textsubscript{2} to concentrations of H\textsubscript{2} and CO at a fixed temperature [5]. The results are shown in Figure 2.6 (a). It can be seen for both H\textsubscript{2} and CO, that the sensitivity increases dramatically for particle sizes less than 6 nm. This sensitivity increase cannot be fully explained by the increase in surface area for small grain sizes. Therefore, the Debye length of the material is an important parameter for understanding the increase in sensitivity for small particle sizes.

Other groups such as Lu et al., have also found that SnO\textsubscript{2} shows an extremely sharp rise in sensitivity for a small particle size [55]. Their sensor results are shown in Figure 2.6 (b). They tested the sensitivity of SnO\textsubscript{2} particle sizes ranging from 2-120 nm for the detection of carbon monoxide. Similarly to Yamazoe, they found that the sensitivity increases sharply for particle sizes less than 10 nm.
Theoretical investigations have also been performed to determine the relationship between sensitivity and particle size for SnO$_2$ [56]. Rothschild et al. developed a model for small particles which states the entire volume of the particle is depleted due to electron trapping at surface states. From there, they calculated the effect that altering the surface-trapped charge density had on the electrical resistance as a function of particle size. Varying the surface-trapped charge density represents the interaction of an analyte gas with the adsorbed oxygen on the surface of the metal-oxide. Their model concluded that decreasing the particle size led to a high sensitivity which they found was proportional to $1/d_m$ [56].
In addition to the findings for SnO₂, other metal-oxides used as gas sensors also displayed an increased sensitivity for a decreasing particle size. Pinna et al. [57] and Korotcenkov et al. [58] have shown this phenomenon using In₂O₃ nanoparticles for the detection of NO₂ and ozone, respectively. Tamaki et al. utilized WO₃ nanoparticles for the detection of NO₂ [59]. They also report this grain-size effect on sensitivity.

This particle-size effect is presented in an ideal manner because there is typically a distribution of particle sizes for the material [60]. While there are several techniques that result in a narrow particle size distribution, such as ball-milling or chemically-aided-milling of the particles, it is highly unrealistic to assume that all of the particles in the sensing film are the same size. Metal-oxide particles sizes are generally calculated using x-ray diffraction using the Debye-Scherrer equation for powder diffraction. It should be noted that this method is an average particle size and much literature overlooks the particle size distribution that encompasses the metal-oxide sensing layer.

2.2.2 *Film Microstructure Importance on Gas Sensing*

In addition to the particle size, the microstructure of the film (thickness and porosity) is important for the sensitivity and response and recovery times of the gas sensor devices [7]. Up to this point, the description of the microstructure of the metal-oxide film has been largely simplified. The electron motion between particles described previously assumed a fairly simple monolayer of grains in between the electrodes. This is not realistic for gas sensor devices because a large number of metal-oxide particles stack together to form a sensing layer [5]. This metal-oxide sensing layer or film will have some porosity that is dependent on the particle size, type of deposition method used, and
temperature/time combination to which the particles have been exposed. Oxygen and the analyte gas diffuse into the film through pores in order to react with the surface and adsorbed oxygen ions, respectively.

In order to have a short response and recovery time, a fast diffusion rate for the oxygen and analyte gas through the pores is critical. This diffusion rate depends on the mean pore size of the metal-oxide sensing layer and the operating temperature of the device [7]. The thickness of the film is also important because particles far away from the surface may be inaccessible for oxygen and the analyte gas if there is not open porosity (connected pores) throughout the sensing layer [61]. Therefore, a thin layer of metal-oxide particles with a large mean pore size leads to increased gas diffusion through the sensing film. For optimum sensor performance, there is a balance that must be achieved because the pores need to be large enough for fast diffusion of gas molecules, but the large pores decrease the surface-to-volume ratio of the sensing film for particles of the same size [27]. Nanoparticles have a high surface area, but a sensing film constructed of nanoparticles has small pores which limits diffusion of the gas molecules. Different gas diffusion processes occur depending on the pore size of the metal-oxide sensing film. For pores in the size range from 4 and 100 nm in diameter, Knudsen diffusion is dominant [5]. Knudsen diffusion of gas molecules without external pressure is given by equation 2.7.

\[
D_k = \frac{4r}{3} \sqrt{\frac{2RT}{\pi \cdot M}}
\]  

(2.7)
In equation 2.7, $D_K$, is the Knudsen diffusion coefficient, $r$ is the pore radius, $R$ is the universal gas constant, and $M$ is the molecular weight of the gas molecule [27]. This equation shows that the diffusion of the gas molecules increases for an increase in pore radius size. Molecular diffusion occurs for pore sizes below 4 nm and surface diffusion prevails for a pore sizes above 100 nm [5]. Deposition methods for creating a film of metal-oxide particles such as screen-printing or sol-gel processing results in pores of various sizes, which make diffusion analysis difficult. In order to study the diffusion of gas molecules through the film, a well-defined particle size, pore size, and thickness must be controlled in the sensing layer.

As previously discussed, sensitivity increases abruptly when metal-oxide nanoparticles are on the order of twice the space-charge layer [62]. This is typically in the several nanometer range. At this size scale, however, the driving force for the aggregation of nanoparticles becomes large due to the van der Waals attraction between particles. The van der Waals attraction is inversely proportional to the particle size [63]. As a result, metal-oxide nanoparticles (primary particles) want to come together, agglomerate, and form larger particles sometimes denoted as secondary particles. These secondary particles are on the order of microns in size. Gas sensing properties are greatly affected by the agglomeration of nanoparticles in the film because only particles near the surface are available for the gas sensing reaction [64]. A diagram of this is shown in Figure 2.7 [5].
Figure 2.7: Schematic of agglomeration of primary particles into secondary particles and resulting gas sensitive region (image from Yamazoe [5]).

When nanoparticles agglomerate and form secondary particles, a high sensitivity is difficult to achieve because the resistance will only change near the surface of the secondary particles in the region labeled gas sensitive region in Figure 2.7. Also, gas diffusion will be constricted to the macro-pores of the sensing layer and the high surface area of nanoparticles will not be utilized. This will lengthen the response and recovery times for the sensor device. Experiments have been performed on the gas sensing capabilities of metal oxide nanoparticles vs. films of larger size particles, and it was found the microstructure of the metal oxide layer is very important for sensitivity and device performance [65, 66].

The agglomeration of metal-oxide nanoparticles is a major obstacle for creating highly sensitive devices. There are many deposition techniques that are used to obtain a thin porous layer of nanoparticles for the sensing film. These include sol-gel [5],
chemical vapor deposition (CVD) [30], and ink-jet printing [67]. Conventional screen printing methods for thick film formation generally lead to agglomeration of the metal-oxide nanoparticles.

2.3 Metal-Oxide Nano-structures for Gas Sensing

Besides metal-oxide nanoparticles, numerous particle morphologies have been fabricated to increase the performance of gas sensor devices. In order to enhance the gas sensitivity, nanostructures with high surface area and full electron depletion are advantageous [68]. Taking this into consideration, various metal oxide nanostructures have been explored, including nanowires [21, 69-71], nanorods [72], nanotubes [9], nanobelts [73], nanosheets [74], and nanocubes [75]. Each of these structures has benefits of high surface to volume ratio as well as features close to the Debye length. However, nanostructures at this size scale suffer from strong van der Waals attraction and agglomeration may develop. The goal of these nanostructured metal-oxides is to avoid the negative effects associated with secondary particle formation, but keep the positive effects of higher sensitivity and short response and recovery times. Two such nanostructures include metal-oxide hierarchical structures and hollow spheres which are fully described in the following sections.

2.3.1 Hierarchical Structure

Metal-oxides with a high surface area and defined porous architecture are being synthesized and deposited as the sensing layer to improve the performance of gas sensor
devices. These are known as hierarchical nanostructures which are assembled from nano-building blocks such as nanoparticles, nanowires, or nanorods, [62, 76, 77]. The hierarchical metal-oxide structures have a high surface area for reaction of the analyte gases and large pores for fast gas diffusion into the sensing film [62]. The van der Waals attraction between these hierarchical structures is small because the structures are in the micron size range. This decreases the driving force for agglomeration in these structures. A direct comparison on sensor performance between metal-oxide hierarchical structures and agglomerated nanoparticles was performed by Kim et al. [78]. Their group created SnO$_2$ micron size particles with nanostructured features using a hydrothermal synthesis procedure. Although the formation mechanisms are not completely understood for the hydrothermal reaction, hierarchical spheres of SnO$_2$ can be synthesized from a reaction between SnCl$_2$, hydrazine, and NaOH [62]. They compared these hierarchical SnO$_2$ spheres to dense agglomerated SnO$_2$ nanoparticles for the detection of ethanol under the same background environment. The results of the sensor tests as well as an SEM image of the hierarchical spheres are shown Figure 2.8.
Figure 2.8: Sensor results of hierarchical SnO$_2$ spheres compared to dense agglomerated SnO$_2$ spheres for the detection of ethanol. An SEM micrograph of the microstructure of the SnO$_2$ hierarchical spheres is shown to the right. (image from Kim [78]).

The hierarchical SnO$_2$ spheres show a much higher sensitivity to a specific concentration of ethanol than the SnO$_2$ agglomerated spheres. The hierarchical spheres also have a much shorter response and recovery time compared to the agglomerated SnO$_2$ nanoparticles. One reason for this is the hierarchical spheres had a surface area of 46.4 m$^2$/g and the agglomerated spheres had a surface area of 34.7 m$^2$/g [78]. The sensing film of hierarchical spheres also had pore sizes ranging from 4 to 100 nm which allowed gas diffusion to take place quickly through the material. This demonstrates that hierarchical nanostructures provide a high surface-to-volume ratio for gas sensing without sacrificing porosity of the film for effective gas diffusion [62].
Other hierarchical structures have been synthesized which show increased sensitivity and short response and recovery times as well. Gou et al. synthesized porous nanostructures of Fe$_2$O$_3$ by a hydrothermal synthesis method and performed gas sensor tests to several reducing gases [79]. The sensitivity to ethanol in the range of 50-1000 ppm was 5-10 fold higher than commercial Fe$_2$O$_3$ powder. Ponzoni et al. found that hierarchical WO$_3$ structures could be formed by thermal evaporation of tungsten powders [80]. When exposed to 50 ppb of NO$_2$ at 300°C, these WO$_3$ hierarchical structures had a 6 fold increase in resistance which is very significant to an oxidizing gas in the parts per billion range. A schematic of the different hierarchical structures that can be created from different nano-building blocks is shown in Figure 2.9 [62]. The trend of surface area and pore size is also denoted in the schematic. For optimum sensor performance, a balance between the surface area and porosity must be determined as described previously.

![Hierarchical structures](image)

**Figure 2.9:** Hierarchical structures with different nano-building blocks and the corresponding trend of surface area and pore size for these structures. (image from Lee [62]).
An experimental study by Choi et al. explored the effect hierarchical particles had on gas sensor response by testing Co$_3$O$_4$ agglomerated nanoparticles, nanosheets, nanorods, and nanocubes to ethanol gas [81]. Each of the nano-structures was synthesized through solvothermal synthesis methods and the microstructure of the metal-oxide films was documented. A comparison of the gas sensor results for each of the hierarchical particles is shown in Figure 2.10 [81]. From the gas sensor result profile, it is clearly evident that the nano-structures incorporating nanosheets, nanorods, and nanocubes outperformed agglomerated nanoparticles in both gas sensor response and faster sensing. The response and recovery times for the hierarchical particles are much shorter than the response and recovery times for the agglomerated nanoparticles. This experimental work led to a conclusion that the particle size is not the only factor for gas sensor response; specifically that the microstructure of the metal-oxide film is also critical.
Figure 2.10: Comparison of gas sensor results exposed to ethanol for \( \text{Co}_3\text{O}_4 \) (a) nanosheets, (b) nanorods, (c) nanocubes, and (d) agglomerated nanoparticles (image from Choi [81]).

Although the sensor results for these hierarchical structures display a high sensitivity and short response and recovery times for several metal-oxides to specific gases, there are a few issues that have not been addressed in literature. The stability and associated electronic drift of the hierarchical structures at elevated temperatures for a significant amount of time has not been reported. Also, the microstructure of the hierarchical structures after sensor testing is rarely shown. It is important to inspect the sensing film before and after sensor operation to identify any changes in the microstructure of the film.
regardless of the particle size or morphology. This is important to be able to tune the nanostructure for optimum gas sensor performance.

2.3.2 *Hollow Spheres*

In addition to hierarchical structures, metal-oxide hollow spheres have shown benefits for gas sensing applications because of enhanced surface area and efficient gas diffusion. Important parameters of the hollow structures include the thickness, permeability, and surface morphology of the shell [62]. If the shell is thick and impermeable, the gas sensing reaction will take place at the surface, and will not utilize the inner part of the hollow spheres. Conversely, a porous shell could allow gas molecules accessibility to both the interior and exterior surfaces of the hollow sphere. Oxygen adsorption could take place on both the inner and outer surfaces of the hollow spheres. This would lead to a depletion layer on both sides of the shell as shown in Figure 2.11 [49].

![Figure 2.11: Diagram showing the electron depletion layers on the outer and inner surface of a metal oxide hollow sphere (image from Zhang [49]).](image-url)
By tailoring the shell thickness to be very small, the entire shell of the hollow spheres become active for the gas sensing reaction [62]. This is equivalent to reducing the film thickness to a value near twice the Debye length in thin-film gas sensors in order to increase the sensitivity and speed of reaction [58, 82]. Metal-oxide hollow spheres can be synthesized in numerous ways which includes the use of a template [46, 83, 84], hydrothermal methods without a template [85, 86], and spray pyrolysis [87].

One of the most cited results involving metal-oxide hollow spheres is from gas sensor measurements performed at NIST by Martinez and Semancik [84]. They developed three different films of SnO₂ and Sb:SnO₂ on micro-hotplate devices and tested them at 400°C for the detection of methanol. The films were made from Sb:SnO₂ hollow spheres after a burn-out of a polymer template, an SnO₂ film generated by chemical vapor deposition, and an Sb:SnO₂ film made from nanoparticles. The sensor data for these three films on micro-hotplate substrates is shown in Figure 2.12 [84].
Figure 2.12: Comparison of sensitivity to methanol for hollow Sb-SnO$_2$ spheres, SnO$_2$ film produced by chemical vapor deposition, and Sb:SnO$_2$ micro-porous nanoparticle film (image from Martinez [84]).

The film made from Sb:SnO$_2$ hollow spheres showed a much higher sensitivity compared to the other two films, which were based on nanoparticulate films without the hollow structure. In an experiment by Zhang et al. comparing SnO$_2$ hollow spheres and SnO$_2$ particles, the group showed the response times of SnO$_2$ hollow spheres to all NO$_2$ concentrations are shorter than those of SnO$_2$ particles [49]. All the recovery times of the SnO$_2$ hollow spheres were no more than 10 seconds, while the recovery times of SnO$_2$ particles were greater than 15 minutes. Park et al. also showed the benefit of metal oxide hollow spheres compared to particles for Co$_3$O$_4$ [88]. They showed that Co$_3$O$_4$ hollow
spheres were more sensitive to acetone than commercial cobalt oxide powders. They attributed this to the higher surface-to-volume ratio of Co$_3$O$_4$ hollow spheres.

The results presented display the high sensitivity and fast response and recovery times by utilizing metal-oxide hollow spheres [62]. Quick gas diffusion to the sensing surface due to porous and thin shells of the hollow structures results in very short response times. Both hollow spheres and hierarchical structures show better performance than films made from metal-oxide particles. A recent journal article (2009) by Choi et al. compares the gas sensor properties of three different forms of In$_2$O$_3$ particles to carbon monoxide [89]. The three different particle morphologies are agglomerates of nanoparticles, hollow spheres, and hierarchical spheres. The sensor properties are shown in Figure 2.13.

![Figure 2.13](image)

**Figure 2.13**: (a) Sensitivity ($R_\text{g}/R_\text{a}$) of In$_2$O$_3$ agglomerated nanoparticles, hollow spheres and hierarchical structures to varying concentrations of CO. (b) Response times and (c) recovery times for the structures are also reported (image from Choi [89]).
The important findings from these graphs are the hierarchical and hollow structures both show quick response and recovery to carbon monoxide and the agglomerated nanoparticles do not display this effect. The hierarchical structures have better sensitivity than both the hollow spheres and agglomerated particles. One of the possible explanations for this is the surface area of the hierarchical structures is 30 m²/g compared to 23.6 m²/g for the hollow spheres. The microstructure of the metal-oxide films was not shown, however. Numerous times in literature the microstructure of the metal oxide layer or film is not reported or taken into consideration. This is an important parameter for accessibility of the gases and should be performed before and after gas sensing to see if there is a change in microstructure at high gas sensor operating temperatures. Regardless, the development of hierarchical structures and hollow spheres for gas sensor technology is an emerging field that shows much promise for device performance.

2.4 Conclusions from Literature Review and Research Group Findings

As outlined in the previous sections of Chapter 2, there are numerous research groups working on metal-oxide nano-structures for chemiresistive gas sensors. For the last 10 years, there has been increased research in implementing nano-structured metal-oxide films to increase the gas sensor response of the devices to trace amounts of analyte gases. As noted above, there have been some benefits of using nanoparticles both experimentally and theoretically to take advantage of the large surface area and charge depletion in the particles. However, in recent studies, agglomeration of nanoparticulate
films has shown to negatively impact sensor performance compared to hierarchical particles with controlled microstructure. Initial work by our research group also found that metal-oxide nanoparticles would agglomerate after deposition onto alumina sensor substrates using screen printing. A scanning electron micrograph (SEM) of TiO$_2$ nanoparticles which are agglomerated on a sensor substrate is shown in Figure 2.14.

![SEM Image of TiO$_2$ nanoparticles](image)

**Figure 2.14:** TiO$_2$ nanoparticles agglomerated in metal-oxide film deposited on alumina sensor substrate by screen-printing.

Our research group’s experimental results verified other group’s findings of agglomerated metal-oxide nanoparticles after screen printing due to the small particles bonding to form a more energetically favorable state. Previous research by a graduate student, Elvin Beach, in our research group found that by dispersing metal-oxide
nanoparticles in an ink and depositing the material via an ink-jet printer, agglomeration in the metal-oxide film between nanoparticles could be avoided [90]. His dissertation focused on metal-oxide nanoparticle synthesis, ink formulation, and picoliter printing utilizing an ink-jet deposition device. Through the use of an ink-jet printer and suspension rheology, metal-oxide nanoparticulate films could be controlled to restrict agglomeration between the particles. This conclusion was critical to the research conducted in this dissertation and his preliminary work is expanded upon for the application of detecting methane and carbon monoxide for coal mining applications.

There are two primary research areas for chemiresistive gas sensors based on nano-structured metal-oxides that this dissertation explores. The first presented is a study to investigate a new method for creating nano-structured metal-oxide films. This will be achieved by creating a porous network of oxide particles and nanowires through deposition of the particles on a microhotplate substrate and subsequent growth of the nanowires between the particles to create a continuous film between the electrodes. The nanowires will be grown using a gold (Au)-catalyst and at elevated temperature under low oxygen partial pressure. A schematic for a microhotplate with dispersed SnO$_2$ particles with gold on the surface before fiber growth is shown in (a) and (b) in Figure 2.15. The proposed tin oxide nanowire formation to create a high surface area, porous film is shown in Figure 2.15 (c). Experiments carried out for this project study are detailed in Chapter 3.
Figure 2.15: Prior to growth: (a) Microhotplate with dispersed SnO₂ particles and (b) gold on surface of SnO₂ particles. After growth: (c) SnO₂ nanowire formation to create porous film.

The second principle research study is presented in Chapters 4 and 5 to compare gas sensor performance of metal-oxide nanoparticles with a microstructure free of agglomeration to micron size particles and hierarchical particles on microhotplate substrates. Gas sensor literature focuses on the negative aspects of metal-oxide nanoparticles in low gas sensor response and long response and recovery times due to agglomeration between particles. With the ink-jet printing technology to deposit metal-oxide nanoparticles free of agglomeration, this dissertation provides a study in a section of gas sensor technology that has not been explored. It is important to note that these two research studies exploring the benefits of nano-structured metal-oxide films were conducted with the goal to fabricate chemiresistive sensors on miniaturized microhotplate platforms and for detecting methane and carbon monoxide for coal mining applications.
Chapter 3: Growth of Nanowires from SnO₂ Particles using Au Catalyst

The goal to create a nanowire network between particles in order to produce a porous, high surface area metal-oxide film has been presented and diagramed in Figure 2.15. Previous investigations from the Center for Industrial Sensors and Measurements (CISM) at Ohio State conducted growth of SnO₂ nanowires on the surface of a dense SnO₂: CoO pellet using an Au-catalyst [91]. This research project was interested in modifying this technology in order to grow SnO₂ nanowires from SnO₂ particles to create a nano-structured metal-oxide film. The results detailed below explore the experiments needed to transfer the previous technology at CISM to develop the SnO₂ nanowire network. This work was submitted for publication in the peer-reviewed scientific journal, Materials Chemistry and Physics [92]. While the research article is contained in some format below, this dissertation provides more detailed explanations of experimental findings and conclusions determined as part of this study and focuses on the scaling down of this technology for use in miniaturized sensors.
3.1 Introduction

Recently, numerous groups have reported SnO$_2$ nanowire growth on various substrates through thermal treatment in a reducing atmosphere [22, 93-95]. These one dimensional (1-D) nano-structures can be synthesized through several methods including chemical vapor deposition (CVD), metal-promoted vapor growth, and laser ablation [96]. While each technique has advantages and disadvantages, the metal-promoted vapor growth using a vapor-liquid-solid (VLS) mechanism to grow nanowires can be utilized on SnO$_2$ particles in addition to traditional dense substrates [97]. Carney et al. used gold (Au) to promote the growth of SnO$_2$ nanowires on sintered SnO$_2$ pellets based on this type of mechanism [91]. An SEM micrograph of Carney’s work in the CISM group at Ohio State is shown in Figure 3.1. SnO$_2$ nanowires nucleate and are grown at locations of gold particles on the surface of the SnO$_2$ pellet.
In addition to understanding the formation and growth of SnO$_2$ nanowires in specific environments, there has been considerable research in the implementation of these nanowires in gas sensor devices [73, 98-101]. Metal-oxide nanowires have benefits over traditional micron-size oxide particles in gas sensing applications due to a larger surface-to-volume ratio and diameters similar to the Debye length of the metal-oxide [99]. The Debye length is a measure of the electric field penetration depth into the bulk of the material. The small size of the nanowires leads to increased performance for chemiresistive metal-oxide sensors which operate through a change in electrical conductance in the presence of reducing/oxidizing gases [5, 7, 62].
There are additional benefits of using a metal-promoted vapor growth of metal-oxide nanowires for gas sensing. While this was not greatly detailed in the literature review in Chapter 2, the inclusion of noble metals such as Au on the surface of SnO₂ increases the gas sensor response to specific reducing or oxidizing gases [102-104]. This is elevated by the catalytic activity of the noble metal to increase the reaction of the analyte gas with the metal-oxide surface resulting in a change in resistance compared to the sensing film’s baseline resistance in air [5]. Recently, research has begun to explore the advantages of implementing SnO₂ nanowire sensors grown using Au-catalysts in gas sensing experiments [105]. The development of Au-decorated SnO₂ nanowire sensors has the potential to reap the benefits of the noble metal catalytic effects and the large surface-to-volume ratio of nanowires.

The goal of this work was to deposit Au-coated SnO₂ micron-size particles on sensor substrates and grow SnO₂ nanowires from the particles by a thermal treatment under reducing conditions in-situ. The growth parameters for SnO₂ nanowire formation from SnO₂ micron-size particles using a gold catalyst are determined. The SnO₂ particles with Au-SnO₂ nanowires on the surface were then used in gas sensor experiments for detection of carbon monoxide without further modification. After testing, a comparison of the gas sensors performance were made using these nano-structures, SnO₂ micron-size particles, and Au decorated SnO₂ particles without nanowire growth to understand the impact of Au and nanowire formation on gas sensing properties. Details on the characterization experimental parameters given by x-ray diffraction and secondary electron microscopy are given in Appendix A of this document.
3.2 SnO$_2$ Nanowire Growth from Dense Pellets and Particles

The technology that existed for SnO$_2$ nanowire growth included formation of a dense SnO$_2$:CoO pellet, deposition of gold on the surface via sputtering, and growth at elevated temperature in a low oxygen partial pressure atmosphere. Initial experiments in this research study centered on attempting to transfer this technology to SnO$_2$ particles in order to grow SnO$_2$ nanowires from pure SnO$_2$ particles using an Au-catalyst. This was achieved by changing the particle preparation, gold deposition technique, and lowering the growth temperature in order to achieve nanowire growth on SnO$_2$ particles instead of SnO$_2$:CoO sintered pellets.

3.2.1 Au-Deposition on SnO$_2$:CoO pellets

Following previous technology from Carney et al.’s process, commercial SnO$_2$ (-325 mesh) was used from Sigma Aldrich and this was ball milled with 5 wt.% CoO particles from Sigma Aldrich. The powder was uniaxially pressed into 2 gram pellets at a pressure of 2000 psi. The samples were subjected to thermal treatment at 1300°C for 24 hours in order to produce a sintered dense pellet. A gold sputtering system was used to deposit gold on the surface of the SnO$_2$:CoO pellet for a total time of 50 seconds. The gold sputter deposition was performed using a Polaron SEM Coating System from Energy Beam Sciences. Post deposition, a thermal treatment was performed at 750°C for 2 hours in order to de-wet the sputtered gold film to form gold particles. A backscattered electron
microscopy (BSE) image of the surface of a SnO$_2$:CoO pellet after the de-wetting procedure is shown in Figure 3.2.

Figure 3.2: BSE micrograph of sputtered gold on surface of SnO$_2$:CoO sintered pellet after de-wetting procedure.

The BSE micrograph in Figure 3.2 provides topological information for the SnO$_2$:CoO pellet with gold on the surface. Backscattered images provide atomic number contrast with higher atomic number elements appearing brighter in the electron micrographs. Lower atomic number elements which are inherently lighter in atomic mass appear darker in BSE images. Therefore, the bright spots in Figure 3.2 are the Au particles which form after the de-wetting thermal treatment of the sputtered gold film. The gold particles on the surface of the SnO$_2$:CoO pellet are smaller than one micron in
diameter, and vary in size. These gold particles are the locations of SnO$_2$ nanowire nucleation and growth which will be discussed in Section 3.2.3. However, for the application of growing SnO$_2$ nanowires from micron and sub-micron size SnO$_2$ particles, the diameter of the gold particles is fairly large. Also, the goal of this work is to have growth from all sides of the SnO$_2$ particles; not to only have growth on the surface of the film. For these reasons, a new gold deposition technique was investigated to deposit very small size gold particles on the surface of SnO$_2$ particles.

3.2.2 *Au-Deposition on SnO$_2$ Particles*

The same commercial SnO$_2$ particles used to create the pellets were heat treated at 1300°C for 24 hours to create micron-sized particles. These micron-size particles were used in all of the subsequent experiments which included being used unmodified as the metal-oxide film in the gas sensor experiments. The initial SnO$_2$ micron-size particles without gold addition were characterized using XRD with the results shown in Figure 3.3. This XRD pattern confirms the cassiterite phase of SnO$_2$ and displays preferred orientation of the (211) plane. The narrow broadness of the diffraction peaks in Figure 3.3 confirms the large (> 1 μm) size of the SnO$_2$ particles.
The micron-size particles of SnO$_2$ were coated with Au using a wet chemistry process which is similar to that used for depositing Au on the surface of TiO$_2$ particles [106, 107]. This process consisted of adding 0.01 g of HAuCl$_4$ to 60 ml of deionized water while stirring. Next, 0.266 g of SnO$_2$ was added to the solution and stirred for ten minutes creating a suspension of SnO$_2$ particles. In a separate beaker, 0.02 g of NaBH$_4$ was added to 60 ml of deionized water while stirring. The NaBH$_4$ solution was slowly added to the Au-SnO$_2$ suspension over three minutes. This was stirred for 30 minutes, filtered,
washed with deionized water, and dried to collect the SnO$_2$ powder with gold on the surface. Gold and chloride ions are present in the suspension of SnO$_2$ particles, and the addition of sodium borohydride solution serves as a reducing agent for the gold ions. The sodium borohydride reduces the Au$^{3+}$ ions into metallic gold particles (Au). The stirring of the suspension is important to promote adhesion of the gold particles onto the surface of the SnO$_2$ particles.

Gold deposited on the surface of the SnO$_2$ particles using the wet chemistry method is shown in an SEM micrograph in Figure 3.4. The micrograph shows the small gold particle size (less than 50 nm), and several gold nanoparticles agglomerated together resulting in non-uniform coverage with areas of higher gold concentration. This location and agglomeration of the gold nanoparticles is critical since these locations are the nucleation sites for the SnO$_2$ nanowires and control network formation.

Figure 3.4: SEM micrograph of Au on surface of SnO$_2$ micron-size particles.
Gold deposition via the wet chemistry technique described previously was also performed on the -325 mesh commercial SnO₂ particles that were not subjected to a heat treatment to make them “micron size”. A designation of -325 mesh size corresponds to the particles passing through a sieve with a specified opening. For -325 mesh, this guarantees that the particles can be no larger than 44 μm, but the SnO₂ commercial particles used were less than 1 micron after SEM investigation. These SnO₂ particles were considered “sub-micron”, and a BSE image after gold deposition is shown in Figure 3.5. From the BSE micrograph, small gold particles are evident as bright spots on the surface of the SnO₂ particles.

**Figure 3.5**: BSE micrograph of Au particles on surface of SnO₂ sub-micron size particles.
The wet chemistry technique was useful in developing a method to deposit gold particles on the surface of both micron and sub-micron size SnO₂ particles. This deposition method was beneficial because it provided a means to synthesize gold nanoparticles on all of the surfaces of the SnO₂ particles. The gold sputtering system used in the previous technology was not applicable for our application and the wet chemistry gold deposition was developed. However, there are a few drawbacks using this technique.

The first issue is the amount of gold deposited on the surface of the SnO₂ particles is difficult to control. Increasing the amount of the gold precursor, during synthesis does increase the amount of gold deposited, but not all of the gold ends up adhering to the particles. The other difficulty in using the wet chemistry technique is the gold particles do not deposit in a uniform manner. There is not any control over the location of the gold particles on the surface of the SnO₂ particles. The location of the gold particles is important because these are the nucleation sites for SnO₂ nanowire growth. Even with these drawbacks of the wet chemistry technique, the gold deposition was suitable for nanowire growth, and this is described in the next section.

3.2.3 SnO₂ Growth on Pellets and Particles

The previous technology from Carney et al. for growing SnO₂ nanowires on the surface of SnO₂:CoO pellets involved a reaction at a temperature between 700-800°C in a humid 5%:95% H₂:N₂ mixture for 1-4 hours [91]. The growth involved placing the sample in a horizontal tube furnace equipped with a mass flow controller (MFC) for
regulation of the environment during growth. The humid mixture was introduced by bubbling the 5%/95% H\textsubscript{2}/N\textsubscript{2} gas through water at room temperature prior passing through the furnace. A constant flow rate of 1 liter/minute (L/min) was used for all growth experiments.

The group at CISM determined these were the proper growth parameters for SnO\textsubscript{2} nanowires on SnO\textsubscript{2}:CoO pellets using an Au-catalyst through experimental trials and theoretical calculations. Their findings were replicated to ensure that SnO\textsubscript{2} nanowires could be grown from the SnO\textsubscript{2}:CoO pellet. An SEM micrograph of the results from this validation test is shown in Figure 3.6. Nanowires can be seen in the image grown from the surface of the SnO\textsubscript{2}:CoO pellet.

![SEM micrograph of SnO\textsubscript{2} nanowires grown at 720°C for 4 hours in a humid H\textsubscript{2}/N\textsubscript{2} mixture.](image)

**Figure 3.6**: SEM micrograph of SnO\textsubscript{2} nanowires grown at 720°C for 4 hours in a humid H\textsubscript{2}/N\textsubscript{2} mixture.
In order to transfer this growth on the surface of SnO$_2$:CoO pellets to SnO$_2$ micron-size particles, the growth temperature had to be decreased from 720 to 600°C. The humid H$_2$/N$_2$ mixture was not modified from the original settings of bubbling through water at a flow rate of 1 L/min. This provides a reducing atmosphere with low oxygen partial pressure for the growth to take place. SnO$_2$ nanowires were grown from SnO$_2$ particles and an SEM micrograph of the SnO$_2$ nanowires is shown in Figure 3.7 (a) which shows a gold cap at the tip of the nanowire which was originally on the surface of the SnO$_2$ particles. This is confirmed by the bright cap at the end of the nanowire displayed in a backscattered electron image in Figure 3.7 (b).

![Figure 3.7: (a) SEM micrograph of SnO$_2$ nanowires thermally grown on SnO$_2$ particles using an Au catalyst and (b) BSE image of Au on tip of SnO$_2$ nanowires.](image)
Evidence of gold at the tip of the SnO$_2$ nanowires is verification of the vapor-liquid-solid (VLS) growth method. The VLS growth of SnO$_2$ nanowires using an Au catalyst follows similar principles to silicon (Si) 1-D nanowire growth performed by VLS [108-110]. The Au-Sn phase diagram is similar to that of the Au-Si phase diagram in that both have a low eutectic melting temperature which is beneficial for utilizing the VLS growth method for these systems. A diagram of Si 1-D nanowire growth by the VLS mechanism utilizing an Au-catalyst from Joyce et al. is shown in Figure 3.8 [110].
As stated previously, the binary phase diagram for the Au-Si system is similar to that of the Au-Sn system. The small gold particles on the surface of the SnO$_2$ particles
undergo Ostwald ripening during the growth treatment [108]. This localizes the gold particles and develops an area where a liquid alloy droplet of Au-Sn is formed. Pure gold melts at a temperature greater than 1000°C under standard conditions, but Au-Sn liquid droplets can form at temperatures near 300°C due to a Eutectic melting in the Au-Sn system [111]. The binary phase diagram for the Au-Sn system is shown in Figure 3.9.

![Figure 3.9: Au-Sn binary phase diagram (image from Okamoto [111]).](image)

The growth mechanism under consideration for SnO$_2$ nanowires on SnO$_2$ particles using an Au-catalyst is slightly more complex than 1-D Si nanowire growth since the oxide is necessary both for the growth and for the application of chemiresistive sensors.
The Au-Sn phase diagram does not encompass the entire experiment because because the thermodynamic stability of the SnO\textsubscript{2} must also be considered in a reducing atmosphere. At the growth temperature of 600°C, liquid Au-Sn droplets develop on the surface of the SnO\textsubscript{2} particles and are located at the tip of the SnO\textsubscript{2} nanowires verifying the VLS mechanism. The vapor source to grow the nanowires must be determined from to the low oxygen partial pressure in the growth chamber.

Carney et al. determined that SnO was the dominant vapor species for the same reducing conditions (5\% H\textsubscript{2}/N\textsubscript{2} humid mixture) at 720°C for growth of SnO\textsubscript{2} nanowires from a sintered SnO\textsubscript{2} pellet [91]. They performed thermodynamic calculations to indicate that SnO gas was the dominant tin bearing species compared to Sn vapor at this oxygen partial pressure. The temperature for growing nanowires from the SnO\textsubscript{2} micron-size particles in this work was decreased from 720°C to 600°C to prevent the SnO\textsubscript{2} particles from reducing to metallic tin. Experiments were conducted at the previous growth temperature of 720°C, but the metal-oxide turned to a grey color and x-ray diffraction determined metallic tin (Sn) was formed. This is due to the higher surface energy of the micron-size particles compared to Carney et al.’s sintered SnO\textsubscript{2} pellet. At growth temperatures lower than 600°C, SEM investigation provided no evidence of SnO\textsubscript{2} nanowire growth. The lower temperature did not provide enough energy to either form Au-Sn droplets on the surface or provide a reducing atmosphere for the SnO gas to re-condense into the Au-Sn droplet. In addition, the importance of oxygen in nanowire growth of SnO\textsubscript{2} nanowires has been explored using pulsed-laser deposition and our findings verify this work’s conclusions [112].
The SnO vapor adsorbs on the surface of the Au-Sn liquid droplets and diffuses into the droplet. At a high concentration of SnO vapor, supersaturation and nucleation occurs at the liquid/solid interface leading to SnO nanowire growth. Additional oxygen is supplied to the fiber tip by the bulk SnO₂ particle since SnO₂ is an n-type oxygen deficient oxide though which oxygen anion transport can occur. At 600°C, additional oxygen required for the conversion of SnO(g) into SnO₂ at the nanowire tip could have been provided by the solid-state diffusion of oxygen from the substrate through the SnO₂ nanofiber or from the gas-phase oxygen.

In addition to the temperature and oxygen partial pressure during growth, the amount of time during the growth treatment is important for the length of the SnO₂ nanowires. SEM micrographs displaying the effect of time on the length of nanowires are shown in Figure 3.10. The sample in Figure 3.10 (a) was only reacted for 30 min. at 600°C while sample in Figure 3.10 (b) was reacted for 2 hours at the same temperature. The average diameter of the SnO₂ nanowires was 52 nm with lengths over 1 micron depending on the reaction time. The longer reaction time allows for more SnO vapor to adsorb on the liquid droplet and develop into longer SnO₂ nanowires.
Figure 3.10: SEM micrographs of SnO₂ nanowires grown on micron size SnO₂ particles at 600°C for (a) 30 minutes and (b) 2 hours.

The growth of SnO₂ nanowires from micron-size SnO₂ particles has been presented with the key modification was a lowering of the growth temperature from 720°C to 600°C in a low oxygen partial pressure atmosphere. Experiments were conducted on the sub-micron size SnO₂ particles with the gold deposited using the wet chemistry technique at a series of temperatures. Growth temperatures above 500°C resulted in a partial reduction of the SnO₂ particles to metallic Sn. Growth temperatures below 500°C did not create any SnO₂ nanowires from the gold particles on the surface of the sub-micron SnO₂ particles. X-ray diffraction confirmed the reduction to metallic tin for some of the SnO₂ particles for growth temperatures above 500°C, and this is shown in Figure 3.11.
Figure 3.11: X-ray diffraction plot showing the submicron SnO$_2$ particles “pre-test” (prior to the growth treatment) and “post test” (after the 600°C growth treatment). The * on the XRD plot signifies a metallic Sn peak and all others correspond to cassiterite.

The XRD plot for the sub-micron SnO$_2$ particles prior to the growth conditions (600°C, low oxygen partial pressure) depicts the cassiterite phase of SnO$_2$ which is completely metal-oxide. After the growth experiment, XRD confirms that part of the oxide has converted to metallic tin. This is not desired for chemiresistive metal-oxide sensors because the tin could provide metallic contact between the electrodes and provide a means of electron transport across the film that would make the device inoperable. SnO$_2$ nanowires were not grown from sub-micron SnO$_2$ particles as part of this research,
but using the principles developed as part of this study, it is possible with careful control of the oxygen partial pressure (reducing environment) and temperature during the growth reaction. Even though nanowire growth was not completed on SnO$_2$ sub-micron size particles, the nanowires grown on the micron-size particles were used for gas sensor testing to determine if the nano-structure development increased gas sensor response of the material to carbon monoxide gas.

### 3.3 Gas Sensor Testing

The creation of SnO$_2$ nanowires from micron-size SnO$_2$ particles provided an interesting possibility to form a porous network for chemiresistive gas sensor testing. Gas sensor testing experiments were conducted to determine if the growth of SnO$_2$ nanowires from SnO$_2$ particles resulted in increased gas sensor response to carbon monoxide compared to the material without growth. Three SnO$_2$ samples were fabricated to compare the gas sensor properties of SnO$_2$ micron-size particles, SnO$_2$ micron-size particles with gold on the surface, and SnO$_2$ nanowires grown with an Au-catalyst from SnO$_2$ micron size particles. The three samples are presented in Table 3.1.
Table 3.1: Sample description for the three samples subjected to gas sensor testing to carbon monoxide.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Material</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>SnO₂ micron-size particles</td>
<td>Commercial SnO₂ particles heated to 1300°C for 24 hours</td>
</tr>
<tr>
<td>Au-SnO₂</td>
<td>SnO₂ with Au deposited on surface</td>
<td>Wet chemistry gold deposition on surface of SnO₂ micron-size particles. No growth of nanowires</td>
</tr>
<tr>
<td>Au-SnO₂ nanowires</td>
<td>SnO₂ nanowires grown on SnO₂ particles via Au-catalyst</td>
<td>Au-SnO₂ sample grown at 600°C for 2 hours under humid H₂/N₂ mixture</td>
</tr>
</tbody>
</table>

3.3.1 Sensor Preparation and Thick-film Gas Sensor Testing Facility

The three samples were fabricated for gas sensor testing on alumina sensor substrates with interdigitated platinum electrodes purchased from the Electronics Design Center at Case Western Reserve University. These alumina sensor substrates were shown in Figure 1.2. All three samples were thoroughly mixed in a cellulose-based organic paste and deposited using a screen-printer (Aremco, Model 3230-B) onto the alumina substrate to create a thick-film to serve as the sensing layer. Conductive wire and paste was attached to the platinum regions on the alumina sensor substrates in order to measure the resistance of the samples. The samples were heat treated at 850°C for 15 minutes to create a firm connection between the conductive wire and platinum. One of the samples with Au on the surface of the SnO₂ particles was exposed to the growth conditions described above to grow SnO₂ nanowires in-situ on the alumina sensor substrate.
Gas sensor testing was performed in a tube furnace with mass flow controllers (MFCs) for control of the environment in the gas sensing chamber. An Agilent LXI Data Acquisition unit was used for recording the resistance of the SnO$_2$ samples. A customized LabVIEW program was used for automation of the gas sensor tests. The program controlled the gas delivery of the MFCs, temperature of the furnace, and the Agilent unit. The samples were tested at a total flow rate of 2 L/min to specific concentrations of CO in a background of dry air. Response values and 90% response and recovery times were calculated by taking average of three signals. A diagram of the gas sensor testing facility used for these tests is shown in Figure 3.12.

**Figure 3.12:** Schematic of gas sensor testing facility used for acquiring data from the SnO$_2$ gas sensor tests.
3.3.2 **Gas Sensor Performance**

The three sensor samples (made of SnO$_2$, Au-SnO$_2$, and Au-SnO$_2$ nanowires) were tested to a specific concentration of CO at elevated temperatures to determine the change in the resistance when exposed to the analyte gas. Raw data of resistance vs. time is shown in Figure 3.13 at 450°C for the Au-SnO$_2$ nanowire sample when exposed to 250 and 500 ppm of CO. The resistance in the background of air ($R_a$) decreases when the analyte gas is introduced and reaches a stable value in the presence of CO ($R_g$). When the analyte gas is removed from the sensing chamber, the resistance increases to the original value in air ($R_a$). This follows an n-type semiconductor behavior and values of response and transient properties such as 90% response and recovery times can be calculated from these tests. Here the response is defined as $R_a/R_g$ and response and recovery times are the times it takes for the resistance to reach 90% of the baseline in air or gas.
Gas sensor tests for the three samples were performed to a fixed concentration of 500 ppm of CO as a function of temperature to determine the optimum temperature where the response for each material was the largest. The gas sensor response which was calculated from these tests for each sample is shown in Figure 3.14. The Au-SnO₂ nanowire sample displayed the largest response of the three sensors with the highest response occurring at 450°C. The response for the Au-SnO₂ sample was the highest at 450°C as well. The
SnO₂ samples without any gold on the surface or nanowires displayed the lowest response of the three materials. The largest response for this sample was at 550°C.

Figure 3.14: Plot of gas sensor response as a function of temperature for SnO₂ and Au-SnO₂ films when exposed to 500 ppm CO.

This reinforces the fact that Au-decorated SnO₂ particles possess better sensor response than SnO₂ particles without a noble metal catalyst on the surface. This is due to the chemical or electronic sensitization that occurs at the Au/SnO₂ interface which promotes a larger transfer of electrons resulting in a greater relative decrease in the overall resistance of the film in the presence of CO. When analyzing the data of the Au-SnO₂ sample vs. the Au-SnO₂ nanowire sample, the nanowires provide a larger gas
sensor response compared to the sample without nanowires. The nanowires increase the surface-to-volume ratio of the sensing film, and this allows more reaction sites for the analyte gas to interact with chemisorbed oxygen ions on the surface of the SnO₂.

Transient properties (response and recovery times) were calculated for all three samples at the optimum temperatures for sensor response to 500 ppm of CO. These results are shown in Table 3.2. The two samples with gold exhibited shorter response times compared to the pure SnO₂ sample. The recovery times for all three samples are fairly long (greater than 8 minutes). The transient properties of the gas sensors are affected by the porosity/microstructure of the metal-oxide film.

<table>
<thead>
<tr>
<th>Material</th>
<th>Response Time (min.)</th>
<th>Recovery Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>10.5</td>
<td>11.3</td>
</tr>
<tr>
<td>Au-SnO₂</td>
<td>1.4</td>
<td>8.9</td>
</tr>
<tr>
<td>Au-SnO₂ nanowires</td>
<td>6.1</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Table 3.2: 90% response and recovery times for SnO₂ (550°C), Au-SnO₂ (450°C), and Au-SnO₂ nanowires (450°C) when exposed to 500 ppm CO in background of dry air.

The microstructure of the SnO₂ films provides useful information to determine the nanowire coverage and porosity of the Au-SnO₂ nanowire sample compared to the other
samples. An SEM micrograph of the pure SnO$_2$ sensing film on the alumina gas sensor substrate is shown in Figure 3.15.

![SEM micrograph displaying microstructure of micron-size SnO$_2$ particle films on alumina sensor substrates.](image)

**Figure 3.15:** SEM micrograph displaying microstructure of micron-size SnO$_2$ particle films on alumina sensor substrates.

From this micrograph, the particle size in microns is easily distinguishable as well as the porosity of the film. An SEM micrograph of the Au-SnO$_2$ nanowire film which was tested on the alumina substrate is shown in Figure 3.16. The nanowires are grown from several particles in the SnO$_2$ film, and the increase in surface area is clearly evident from the numerous nanowires.
Figure 3.16: SEM micrograph of Au-SnO$_2$ nanowire sample used for sensor testing on alumina sensor substrate.

The three samples were tested to determine the optimum temperature to a fixed concentration of CO. Subsequently, this operating temperature was used to test the SnO$_2$ samples to increasing concentrations of analyte gas, specifically 250, 500, 1000, and 2500 ppm of CO. The gas sensor response values for this fixed temperature sensing test are shown in Figure 3.17. The Au-SnO$_2$ nanowire sample displayed the highest response to all concentrations of carbon monoxide, and the gas sensor response rises for increasing amounts of CO. These concentrations are significant for air quality control of carbon monoxide as elevated levels of CO are toxic to humans.
Figure 3.17: Plot of response vs. CO concentration at a fixed temperature for SnO$_2$ and Au-SnO$_2$ films.

The fixed temperature sensing results in Figure 3.17 reinforce the conclusions deduced in the previous tests. The SnO$_2$ micron-size particles have the lowest gas sensor response of the three samples with the Au-SnO$_2$ sample having slightly higher response. The Au-SnO$_2$ nanowires have the largest gas sensor response due to the increased surface area after nano-structure formation. This was an important conclusion to confirm for three different samples fabricated in the same manner on the same sensor platform. It is difficult to compare samples from literature due to different fabrication procedures and limited availability of information about the microstructure of the samples after testing.
3.4 Conclusions

A new method was created to grow SnO₂ nanowires were grown from SnO₂ particles using an Au catalyst at 600°C under reducing atmospheric conditions on alumina gas sensor substrates in-situ. Gold deposition via a wet chemistry technique was developed and utilized to deposit nanoparticles of gold on the surface of the SnO₂ particles. The SnO₂ nanowires were grown by the VLS mechanism which is confirmed by the Au cap on the tip of the nanowire. The growth temperature had to be lowered from 720°C for previous technology on SnO₂:CoO pellets to 600°C for micron-size SnO₂ particles to prevent reduction of the sample to metallic tin. The nanowires had an average diameter of 52 nm with lengths greater than 1 μm, which can be controlled by the time of reaction. These Au-SnO₂ nanowires were used in gas sensor experiments and had improved performance compared to Au-coated SnO₂ micron-size particles without nanowires and SnO₂ samples devoid of nanowires. The Au-SnO₂ nanowires had the highest gas sensor response to CO gas at 450°C and had superior performance compared to the other two materials.

While this study was critical to explore SnO₂ nanowire growth on SnO₂ particles, there are some drawbacks to the study in regards to the overall goal of this project to develop nano-structured metal-oxide films on miniaturized sensor substrates for detection of carbon monoxide and methane in coal mines. The first is the gas sensor response values for fairly high concentrations of CO are not very large (Ra /Rg < 2.5). The gas sensor response for CO concentrations of interest in coal mining applications is small and a good signal to noise ratio is needed. Also, since there are two reducing gases to detect,
other transition metal-oxides are needed to create a gas sensor array. The wet chemistry deposition method developed as part of this research is applicable for other metal-oxide samples in addition to SnO₂. A BSE image of gold nanoparticles on the surface of sub-micron TiO₂ particles is shown in Figure 3.18.

![BSE image of gold nanoparticles on sub-micron TiO₂ particles](image)

**Figure 3.18:** Backscattered electron micrograph of gold nanoparticles deposited via wet chemistry technique on sub-micron TiO₂ particles.

Gold deposition on the surface of metal-oxide particles occurs by reducing the gold ions in the presence of the metal-oxide particles in the suspension. The size of the gold nanoparticles is very small (less than 20 nm), and this process is transferrable to other metal-oxide systems. However, other transition metal-oxides such as (TiO₂, ZnO, and NiO) do not form a eutectic with Au, and nanowire formation cannot be performed in this
manner. The growth of other metal-oxide nanowires from particles using a gold catalyst was not developed.

The initial proposed research for this was to grow SnO$_2$ nanowires from SnO$_2$ sub-micron particles or nanoparticles on microhotplate substrates. However, this growth method was not applicable for SnO$_2$ particles of this size scale due to reduction to metallic tin as a result of a higher surface energy of the particles. A deposition method other than screen printing needed to be developed as well in order to deposit the material without damaging the small microhotplate substrate. For these reasons, a new study was conducted to compare metal-oxide nanoparticles, hierarchical particles, and micron-size particles to investigate gas sensor response of the different nano-structured films on miniaturized substrates.
Chapter 4: Metal-Oxide Synthesis and Deposition on Microhotplates

Metal-oxide nanoparticles and hierarchical particles can be synthesized through a variety of techniques including methods carried out in a liquid medium and by vapor phase techniques. Regardless of the synthesis method, the important properties for operation of the metal-oxides in chemiresistive gas sensors are the particle size, morphology, and microstructure of the resulting film on the sensor substrate. This chapter focuses on defining the reasons the metal-oxide nano-structures used in this research were synthesized using hydrothermal and solvothermal techniques for control of particle size, morphology, and breadth of metal-oxides for array development. It also describes why ink-jet printing was utilized as the approach to deposit the metal-oxide nano-structures on miniaturized sensor substrates in the form of microhotplate platforms. Deposition via ink-jet printing has advantages of accuracy at the small size scale of the microhotplates and reproducibility between samples since a controlled amount of material can be deposited at volume levels in picoliters. In order to deposit the metal-oxide nano-structures via ink-jet printing, metal-oxide laden suspensions had to be formulated with specific rheological properties including density, viscosity, and surface tension. A portion of this chapter can be found in the research article published by the author in Science of Advanced Materials [113].
4.1 Introduction

There are two primary steps to create nano-structured metal-oxide films on miniaturized sensor substrates, and there are several different processes to achieve this goal. One route involves synthesizing the material via a specific method and subsequently using a liquid medium to deposit the oxide on a sensor substrate. Metal-oxide nano-structures can be synthesized in a liquid medium by non-aqueous liquid phase reactions [114], hydrothermal [115], solvothermal [88, 116, 117], coprecipitation [118], sol-gel [119, 120], and emulsion-based synthesis techniques [121]. These materials can then be deposited on the sensor platform by screen printing [122], spin coating [123], dropping via micro-capillary [19, 84], or ink-jet printing [67, 124].

The other route is to synthesize the metal-oxide nano-structured material directly on the sensor platform. Methods for the direct synthesis of the metal-oxides on the sensor substrates include physical vapor deposition (PVD) through sputtering or thermal evaporation [125, 126] and chemical vapor deposition (CVD) using metal organic precursors [127-129]. Each technique has advantages and disadvantages, and this was explored extensively in group member, Elvin Beach’s dissertation [90].

Given all the various metal-oxide nano-structure synthesis techniques and methods for depositing on sensor substrates, hydrothermal and solvothermal synthesis and ink-jet printing to form the sensing film was used for fabricating the chemiresistive gas sensors. Hydrothermal synthesis for ceramic processing is defined as an aqueous chemical reaction in a sealed container at a temperature that autogenously generates an elevated pressure [130]. This synthesis method allows the nucleation of metal-oxide nanoparticles
at low temperature (100-350°C), and the particles are fully crystalline and do not require an additional heat-treatment. The solvothermal synthesis technique uses the same processing methods as the hydrothermal version with the only difference being the use of a non-aqueous medium. The benefits of hydrothermal and solvothermal techniques include small particle size distribution, fully crystallized particles with no additional heat treatment required, chemical homogeneity, single step processing, and morphology control [131, 132].

Recently, developments in hydrothermal and solvothermal synthesis methods have led to numerous metal-oxide nanoparticles being created with particle sizes less than 20 nm in addition to hierarchical structures produced with nano-structured features [62, 117, 133-135]. In addition, another advantage of this synthesis method is the wide range of metal-oxide materials (SnO₂, TiO₂, ZnO, NiO, Co₃O₄, etc.) able to be created using this technique which is beneficial for gas sensor array development. Through the use of this synthesis method, the particle size and morphology of the metal-oxides can be controlled and a deposition method to prevent agglomeration of the nanoparticles in the resulting metal-oxide film is also desired.

Ink-jet printing of nanoparticle-laden suspensions has been shown to be effective in controlling the microstructure of the metal-oxide film by restricting agglomeration [90]. Ink-jet printing as presented in this research involves the drop formation of metal-oxide laden inks through the use of a piezoelectric dispensing printhead. The printhead consists of a glass capillary surrounded by a piezoelectric material. Through an applied voltage, the piezoelectric material provides compression on the glass capillary and droplets of
picoliter volume can be produced depending on the orifice of the glass capillary. There are several properties that must be controlled during ink-jet printing including, but not limited to, solids loading, density, viscosity, surface tension, and evaporation rate of the ink as well as printing settings of applied voltage, vacuum level, and orifice diameter. These properties must be regulated to produce consistent drops of a specific volume which corresponds to amount of material deposited on the miniaturized sensor substrate. The physical size of the microhotplate also dictates the positioning of the drops produced by the ink-jet printer must be precise and reproducible.

The motivation behind using hydrothermal and solvothermal techniques for synthesizing metal-oxide nano-structures with definitive particle size and morphology has been presented. Ink-jet printing was used for controlling the microstructure of the deposited metal-oxide film on the miniaturized sensor substrate.

4.2 Hydrothermal and Solvothermal Synthesis of Metal-Oxide Nanoparticles and Hierarchical Particles

The experimental procedures for synthesizing the SnO₂, TiO₂, ZnO, and NiO nanoparticles and SnO₂ hierarchical particles used in the subsequent chapters is described in detail in this section. Characterization of the synthesized metal-oxide nano-structures is presented which led to conclusions regarding the particle size and morphology of the material.
4.2.1 Nanoparticle Synthesis

A series of experiments for synthesizing SnO₂ nanoparticles was performed using a hydrothermal method that is a modification of the technique for creating Sb-SnO₂ nanoparticles [115]. Sn powder (45 μm particle size) and 70% nitric acid (HNO₃) were purchased from Sigma Aldrich (USA, Milwaukee, WI) and used without further purification. The chemicals were mixed in a 45 ml cylindrical Teflon® liner made to fit inside of a stainless steel high pressure acid digestion vessel from Parr Instrument Company (USA, Moline, IL). A picture of the high pressure acid digestion vessel is shown in Figure 4.1. These pressure vessels were used for synthesis of all the metal-oxide nano-structures presented in this dissertation.

Figure 4.1: Teflon®-lined pressure vessel for hydrothermal and solvothermal synthesis.
Twenty milliliters of deionized water was placed in the Teflon® container to which 0.75 grams of Sn powder was added. Ten ml of HNO₃ was slowly added to this mixture in a fume hood, and brown NO₂ gas was given off at the end of the addition process. The contents were sealed and placed in the oven at a temperature ranging from 125-200°C for 12 hrs. The acid digestion vessel was removed from the oven and allowed to cool to room temperature. The precipitates were washed with deionized water for a total of three cycles. For analysis of the SnO₂ nanoparticles, they were dried at 100°C.

The previously published work acknowledged that different sized Sb-doped SnO₂ particles could be made depending on reaction conditions, and expanding on this, the focus was to explore the relationship between the reaction temperature and particle size for pure SnO₂ in order to control the particle size [115]. The reaction mechanism for the formation of SnO₂ is shown in equation 4.1:

\[
4\text{HNO}_3 + \text{Sn} \rightarrow \text{Sn(OH)}_4 + 4\text{NO}_2 + \text{gas} \uparrow
\]

\[
\text{Sn(OH)}_4 \xrightarrow{\text{heat, pressure}} \text{SnO}_2 + 2\text{H}_2\text{O}
\]

The XRD plots obtained from samples synthesized at a range of temperatures from 125°C to 200°C are shown in Figure 4.2.
The diffraction pattern peaks correspond to the cassiterite form of SnO$_2$. These XRD patterns were obtained after washing and drying at low temperature. One of the benefits of using hydrothermal synthesis methods is fully crystalline particles with no additional heat treatment required. The particle size of the SnO$_2$ nanoparticles can be measured from the broadness of the peaks in the XRD pattern. This can be calculated using the Debye-Scherrer equation shown in equation 4.2:

$$B = \frac{0.9 \lambda}{d \cos \theta}$$  \hspace{1cm} (4.2)
where $B$ is the broadening of the diffraction peak measured at the full-width at half maximum intensity, $\lambda$ is the x-ray wavelength, $d$ is the particle or grain size (diameter), and $\theta$ is the angular location of the peak in radians.

The particle sizes calculated using the Debye-Scherrer equation are indicated in Figure 4.2. The calculated particle size of SnO$_2$ synthesized at 125°C was 4 nm, and the particle size increased with temperature to a value of 8 nm at 200°C. Experiments cannot be performed greater than 250°C due to limitations of the acid digestion vessel. This series of experiments proved that the temperature during hydrothermal synthesis of SnO$_2$ during nanoparticle formation can be used to control the particle size over a limited range.

The phase and morphology of the SnO$_2$ particles synthesized in this manner were explored previously using transmission electron microscopy (TEM). A TEM image and selected area electron diffraction (SAED) pattern for SnO$_2$ nanoparticles synthesized at 150°C for 12 hours is shown in Figure 4.3. The TEM micrograph displays the small particle size of the SnO$_2$ nanoparticles although some of the particles are agglomerated on the carbon film in the TEM. In addition, the SAED pattern shows broad diffraction rings indicating small particle size.
Figure 4.3: TEM micrograph and SAED pattern of SnO$_2$ nanoparticles synthesized at 150°C (image from Beach [90]).

The SnO$_2$ nanoparticles used throughout the rest of this dissertation were synthesized using the hydrothermal technique at 150°C for 12 hours. In addition to synthesizing SnO$_2$ nanoparticles, TiO$_2$, 5 mol% Nb-doped TiO$_2$, ZnO, and NiO nanoparticles were synthesized using a solvothermal method that has been reported for various oxides [57, 116, 136] and developed by the research group [117]. The synthesis of these metal-oxide nanoparticles in an organic solvent can take place at low temperature (50-250°C) and the reaction pathways have been studied [133].

For solvothermal synthesis of TiO$_2$ nanoparticles, 5.86 ml of titanium tetraisopropoxide was added to 17.92 ml of 2-butanone in an inert environment in a glove box with humidity and oxygen control [133]. The precursor and solvent was placed in a 45 ml Teflon-lined pressure vessel an placed in an oven at 200°C for 24 hours. After the
reaction was completed, the particles were washed with fresh 2-butanol and isopropanol to remove any unreacted organic material. The TiO$_2$ nanoparticles were dried at 100°C for further characterization. One of the benefits of utilizing this synthesis method is the ability to dope the metal-oxide with other transition metal-oxides. Dopants have been widely used in gas sensor research to increase conductivity of the metal-oxide and improve gas sensor response [1, 5, 64]. In addition to TiO$_2$ nanoparticles, Nb-doped TiO$_2$ nanoparticles can be synthesized by adding the appropriate amount of niobium ethoxide prior to the reaction. Five mol.% Nb-doped TiO$_2$ nanoparticles were created by adding 0.25 ml of niobium ethoxide to the titanium tetraisopropoxide and 2-butanol. XRD results of both the TiO$_2$ nanoparticles and 5 mol.% Nb-doped TiO$_2$ nanoparticles are shown in Figure 4.4.

The XRD data from Figure 4.4 corresponds to the anatase (low temperature) phase of titanium dioxide. The 5 mol.% Nb-doped TiO$_2$ nanoparticles display the same intensity peaks which indicates that the niobium ion has substitutionally replaced the titanium ion in the lattice. This is important for two reasons. The first is there is not any secondary phase formation which can affect the conductivity of the metal-oxide film when these nanoparticles are deposited. Also, the substitutional doping of niobium creates an extra electron available for conduction in the lattice through the formation of an oxygen vacancy. Using Kroger-Vink notation, this is demonstrated in equation 4.3.

\[
Nb \underset{\text{TiO}_2}{\longrightarrow} Nb^\prime_{\text{Ti}} + V_{O}^- + e^\prime
\]  

(4.3)
Figure 4.4: XRD plots of TiO$_2$ nanoparticles and 5 mol.% Nb-doped TiO$_2$ nanoparticles.

The doping of the TiO$_2$ nanoparticles with niobium displays the flexibility of using the solvothermal method for synthesizing the metal-oxide nanoparticles. Thermal gravimetric analysis (TGA) was also performed on the TiO$_2$ nanoparticles for analysis on the content of organic remaining on the material. The TGA analysis involved heating the TiO$_2$ nanoparticles to 1000°C at 10°C/minute and recording the weight loss of the sample as a function of temperature. The TGA plot for the TiO$_2$ nanoparticles is shown in Figure 4.5.
In Figure 4.5, the weight loss of the TiO$_2$ nanoparticles is only 2.5%, and this occurs at a temperature less than 400°C. This indicates there is very little organic material left after solvothermal synthesis of the TiO$_2$ nanoparticles. There is very little weight loss at temperatures between 400 and 1000°C confirming that there is not any additional oxide reduction or formation.

In addition to SnO$_2$ and TiO$_2$ nanoparticles, NiO and ZnO nanoparticles were synthesized using solvothermal techniques. The reaction pathway and full details of the NiO nanoparticle synthesis is provided by Beach et al. in *Materials Chemistry and*
Physics [117]. Briefly, 0.5 grams of Ni-acetylacetonate (Ni-acac) was added to 20 ml of 2-butanone, sealed in a 45 ml Teflon-lined pressure vessel and reacted at 200°C for 24 hours. Washing of the NiO nanoparticles was performed with fresh 2-butanone and isopropanol. Zinc oxide nanoparticles were synthesized using a solvothermal technique reported in literature [136]. This process involved adding 1 gram of zinc acetylacetonate (Zn-acac) to 20 ml of benzylamine in a 45 ml Teflon-lined acid digestion vessel. This was reacted at 100°C for 6 hours, allowed to cool, and washed several times with fresh isopropanol. All four metal-oxide nanoparticles (SnO₂, TiO₂, ZnO, and NiO) are subsequently used in the array development described in Chapter 6.

4.2.2 Hierarchical Particles

As defined in the literature review in Chapter 2, hierarchical particles have a morphology consisting of nano-sheets or nano-features combining together to make a larger (in diameter) size particle. Recently, numerous research groups have touted the benefits of utilizing hierarchical metal-oxide particles instead of nanoparticles for improved gas performance. Two different metal-oxide hierarchical materials were synthesized based on published work in literature.

SnO₂ hierarchical spheres were made using a hydrothermal method that displayed sensitivity to ethanol gas [78]. Briefly, 0.225 grams of SnCl₂·2H₂O and 0.4 grams of oxalic acid (H₂C₂O₄) were added to 20 ml of deionized water in the Teflon-lined acid digestion vessel. To this mixture, 418 μl of 80% N₂H₄·H₂O solution was added, and the contents were sealed and placed in the oven at 180°C for 14 hours. The precipitates were washed, dried, and heat treated at 600°C for 2 hours.
An SEM micrograph of the SnO$_2$ hierarchical structure is shown in Figure 4.6. This image displays the large number of surfaces protruding from the center of the particle. The Brunauer, Emmett, and Teller (BET) surface area measurement for the SnO$_2$ microspheres was 54.3 m$^2$/g. These SnO$_2$ particles were used in the gas sensor performance comparison study with SnO$_2$ nanoparticles and micron-size particles presented in Chapter 5.

![SEM micrographs of SnO$_2$ hierarchical particles synthesized by hydrothermal method.](image)

**Figure 4.6:** SEM micrographs of SnO$_2$ hierarchical particles synthesized by hydrothermal method.

### 4.3 Deposition of particles on microhotplate substrates

Hydrothermal and solvothermal synthesis techniques have been described to create metal-oxide nanoparticles and hierarchical particles with an emphasis on controlling the particle size, morphology, and phase of the material. Due to the small physical size of
the microhotplate substrates, a deposition procedure needed to be established to accurately and reproducibly deposit the material on the sensor platforms.

4.3.1 *Ink-jet Printing System*

As described previously, there are a few deposition techniques that are used to obtain a porous layer of nanoparticles for the sensing film. These include sol-gel [5], chemical vapor deposition (CVD) [30], and ink-jet printing [67]. However, there is a disconnect in gas sensing literature between the hydrothermal and solvothermal synthesis of nanoparticles and nano-structures and the integration of these materials on miniaturized sensor substrates. There are numerous challenges for this assimilation of nanoparticles and nano-structures which include microstructure of the film, reproducibility, standardization for multiple metal-oxide materials, and fabrication for large-scale mass production. Miniaturized gas sensors incorporating multiple metal-oxide materials are important for array devices due to the cross-sensitivity of chemiresistive metal-oxide gas sensors. Ink-jet printing is a method for overcoming these challenges. In addition, ink-jet printing is a versatile technique that has been used for depositing metal-oxides for transparent electrodes and thin film transistors [137, 138]. This section is designed to show the advantages of using ink-jet printing as a way to controllably and reproducibly deposit nanoparticles and nano-structures on microhotplate devices with a porous microstructure free of secondary particle formation for applications in gas sensing.

A MicroFab jetLab II ink-jet printer was used as the ink-jet printing system for depositing the material onto the microhotplate platforms. This piece of equipment incorporates a piezoelectric printhead deposition with automation software for control in
depositing the material accurately at small size intervals. Photographs of the ink-jet deposition system are shown in Figure 4.7.

Figure 4.7:(A): MicroFab jetLab II ink-jet printer, (B): printhead over top of microhotplate sensor platform, and (C) printhead with glass capillary next to U.S. dime for size comparison.
In (A), the whole system can be seen with the computer to control the printing software and the multiple cameras to view the drop evolution as well as the stage location. In (B), a microhotplate substrate is attached to the stage and the printhead was placed over top of the sensor platform. In (C), the piezoelectric printhead is shown with a glass capillary orifice diameter of 50 µm next to a U.S. dime for size comparison. The printhead consists of a glass capillary with an orifice of 50 µm surrounded by a lead zirconia titanate piezoelectric tube actuator. The operation of the ink-jet printer was detailed heavily in Elvin Beach’s dissertation which should be consulted for ink-jet printing procedures [90]. The ink formulation and printing procedure was altered for the application of detecting methane and carbon monoxide on microhotplate sensor substrates in this research. Details of the ink formulation and deposition methods are described in the subsequent sections.

4.3.2 Ink Formulation

In order to use the ink-jet deposition system, particle-laden ink suspensions were developed for compatibility with the ink-jet printer. The main requirements of the particle-laden ink are the suspension cannot contain particles large enough to jam/clog the fluid ejection hole and it cannot be too viscous to be printed [139]. Also, the inks must be stable with time, stable in air, and should not build up solid deposits which can lead to inconsistencies during the printing process.

Each ink was formed by mixing 15 ml of 30:70 wt.% water:ethylene glycol solution prior to the addition of the metal-oxide particles. This fluid ratio was used as it possessed the appropriate rheological properties such as viscosity and surface tension needed for
compatibility with the ink-jet printer as well as to prevent rapid evaporation of the ink at the print-head.

After the solution was thoroughly mixed, 1 wt.% Bicine was added to the solution by sonication in a Branson Sonifier Model S-250D with a 1/2” micro-tip. The solution was sonicated for 15 minutes, then 1-2 wt.% metal-oxide powder was added and sonicated for 15 additional minutes. Bicine addition was used as a small particle dispersant to prevent particle agglomeration.

The sonifier (sonicator) produces a high intensity mechanical vibration which is used for homogenizing the ink in order to create a stable suspension. A Polystat R6L chiller and cooling cup is helpful for creating a constant temperature during sonication which typically generates a large amount of heat. Producing an ink with a homogeneous dispersion of solids is important for reproducibility when depositing onto a sensor substrate. A picture of the set up including the sonicator, chiller, and close up of the process for a TiO$_2$ particle-laden ink is shown in Figure 4.8.
Several metal-oxide nanoparticle-laden inks were created for use in the ink-jet printer to deposit on the microhotplate sensor substrates for gas sensor testing. They were all formulated by the experimental procedure above even though the particle size varied slightly between the materials (5-20 nm). Images of five metal-oxide nanoparticle-laden inks are shown in Figure 4.9.
It is important to describe the important rheological properties of the inks that affect the ink-jet printability of the oxide-laden suspensions. With this in mind, the surface tension (\(\gamma\)), viscosity (\(\eta\)), evaporation rate, and drying properties of the liquids used for the oxide suspensions are critical factors for producing porous metal-oxide films.

The most influential work in literature that has been performed on ink-jet printing of particulate suspensions has focused on some dimensionless rheological properties to aid in ink-jet printer compatibility [140, 141]. These dimensionless quantities that are important for the printability of the ink include the Reynolds number (\(\text{Re}\)), Weber number (\(\text{We}\)), and the inverse of the Ohnesorge number (\(\text{Z}^{-1}\)). The Reynolds number is used to relate the inertial forces to the viscous forces. The Weber number is a relationship between the fluids’ inertial forces and surface tension forces. The Ohnesorge number
relates the viscous and surface tension forces of the fluid. The equations for these dimensionless quantities are listed in equations (4.4, 4.5, and 4.6) respectively.

\[
N_{Re} = \frac{vr\rho}{\eta}
\]

\[
N_{We} = \frac{v^2r\rho}{\gamma}
\]

\[
Z^{-1} = \frac{\sqrt{N_{We}}}{N_{Re}} = \frac{\eta}{\sqrt{r\gamma}}
\]

The variables include the drop velocity \( (v) \), the radius of the print-head orifice \( (r) \), and the density of the fluid \( (\rho) \). For a drop velocity of 2 m/s, a print-head orifice radius of 25 μm, and measured values of density, surface tension, and viscosity, these quantities were calculated for fluids as well as nanoparticle-laden inks. The results are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \rho ) (g/cm³)</th>
<th>( \gamma ) (mN/m)</th>
<th>( \eta ) (mPa s)</th>
<th>( N_{Re} )</th>
<th>( N_{We} )</th>
<th>( Z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized Water</td>
<td>1.01</td>
<td>71.8</td>
<td>1.02</td>
<td>49</td>
<td>1.4</td>
<td>41.4</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>1.11</td>
<td>47.2</td>
<td>17.4</td>
<td>3.2</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>30 wt% Water 70 wt% Ethylene Glycol</td>
<td>1.07</td>
<td>53.0</td>
<td>6.3</td>
<td>8.5</td>
<td>2.0</td>
<td>5.9</td>
</tr>
<tr>
<td>2 wt.% SnO₂ nanoparticle 50:70 Water:Ethylene Glycol</td>
<td>1.10</td>
<td>50.5</td>
<td>6.8</td>
<td>8.1</td>
<td>2.2</td>
<td>5.5</td>
</tr>
<tr>
<td>2 wt.% TiO₂ nanoparticle 50:70 Water:Ethylene Glycol</td>
<td>1.09</td>
<td>50.8</td>
<td>6.0</td>
<td>9.1</td>
<td>2.1</td>
<td>6.2</td>
</tr>
</tbody>
</table>

**Table 4.1:** Table of rheological properties for nanoparticle-laden inks.
The ratio of water and glycerol or water and ethylene glycol is important for rheological properties such as surface tension and viscosity of the ink. Water has a high evaporation rate and high surface tension, and glycerol is used as a drying control agent to lower the surface tension and reduce the evaporation rate of the suspension. Ethylene glycol serves the same purpose as glycerol and these two liquids are known as drying control agents or humectants in ink-jet printing literature [139].

A few research groups have reported that the inverse Ohnesorge number is useful to predict printability of a fluid and a suitable range is $Z^{-1}$ from 4-14 [140, 142]. From Table 4.1, the liquid solutions of water and glycerol and water and ethylene glycol fit in this range. Also, the $\text{SnO}_2$ suspension using 5 nm particles synthesized by the aforementioned hydrothermal process falls within this region as well. This demonstrates the versatility of creating nanoparticle suspensions with different metal-oxides and different particle sizes which are compatible with the ink-jet printer.

4.3.3  \textit{Ink-jet Printing of Particle-laden Inks}

The ink-jet printing of the oxide-laden inks occurs through a voltage source applied to the piezoelectric material around the glass capillary. This physically squeezes the glass capillary and results in an ink droplet expelled from the orifice of the printhead. A time-lapse image of this process is shown in Figure 4.10.
Even with careful ink formulation, controllable and reproducible deposition of nanoparticle-laden inks on microhotplate platforms does have some challenges. These include clogging of the print-head, satellite drops, and first drop reliability. Clogging of the orifice on the end of the print-head can occur when large particles block the orifice or agglomeration and settling of the particles in the ink gather at the orifice. A stable ink with a small particle size is important for reproducible drop formation.

Another challenge of ink-jet printing is the jetting parameters for each ink may need to be slightly adjusted to prevent the formation of satellite drops during deposition. Satellite drops occur during the jetting process if the liquid does not break off in one drop when expelled from the orifice. These satellite drops may have a random trajectory leading to poor drop accuracy. This leads to inconsistencies in the printing process. An example of the SnO$_2$ nanoparticle-laden ink deposited on silicon without satellite drops and with satellite drops is shown in Figure 4.11 (a) and (b), respectively, prior to drying.
First drop reliability is a common challenge in micro-drop generation during ink-jet printing as well due to localized evaporation at the surface of the orifice [139]. During stage motion to align the print-head over the microhotplate platform, drop deposition is stopped. When jetting is started again after more than a 10 second down time, the accuracy of the first drop is sometimes unpredictable. To overcome this challenge, drop deposition occurs close to the sensor substrate, and then stopped for alignment to minimize the time when there is not jetting of the ink. This greatly improves the first drop reliability for the deposition of the nanoparticle-laden ink. Examples of nanoparticle-laden inks printed with inaccuracy in the first printed drop are shown in
Figure 4.12. The first drop of the pattern is the lower left droplet. It can be seen from the two drop arrays in the figure that the location of the first droplet for both samples was inaccurate.

**Figure 4.12:** First drop reliability problems for metal-oxide nanoparticle inks which show the first drop (lower left) has inaccuracy compared to the other drops.

With the ink-jet printing challenges defined and a method for overcoming this established, special attention had to be paid to the specific parameters for depositing the oxide-laden inks on the microhotplate substrates. The distance between the electrodes that needed to be covered on the microhotplate platforms was 250 μm. Since the orifice of the printhead is 50 μm, even after spreading of the ink solution on the sensor platform, one drop will not produce an oxide film to cover the electrodes. A series of experiments
were conducted on a silicon substrate for understanding the spreading of the oxide-laden ink and the physical size of particle coverage. Five SEM micrographs are shown in Figure 4.13 which were taken at the same magnification with an increasing number of drops deposited from the ink-jet printer. The diameter of the oxide film coverage is also provided on the SEM micrographs. This shows the film size variability capabilities of the ink-jet deposition system.

![Figure 4.13](image1)

**Figure 4.13:** Metal-oxide nanoparticle ink deposited on silicon with different size coverage due to number of drops deposited. Diameter of metal-oxide film is also indicated on the micrographs.

After testing on silicon substrates, SnO₂, NiO, TiO₂, and ZnO nanoparticle-laden suspensions were printed on the microhotplate platforms. The printing procedure used to achieve metal-oxide coverage of the electrodes was a series of drops at several positions
with the drops overlapping to produce one larger drop. This printing procedure was a 10x10 array with a spacing of 20 μm between printed positions in both the x and y axis direction. Five drops were deposited at each trigger location. Optical images for a SnO$_2$ nanoparticle based deposition on the microhotplate platform are shown in Figure 4.14. The image in (A) was taken using the camera attached to the ink-jet deposition system after printing. The bright field optical image in (B) was taken before heat treatment using a Nikon Eclipse optical microscope. A heat treatment at 350°C for 3 hours was performed to produce the metal-oxide film through evaporation of the water and ethylene glycol from the wet ink. A bright field optical image is shown in (C) in Figure 4.14 which shows the dried SnO$_2$ film on the microhotplate platform with coverage between the two gold electrodes.

**Figure 4.14**: SnO$_2$ nanoparticle film produced by ink-jet deposition. (A) Image taken from the camera attached to the ink-jet printer, (B) bright field optical image taken with wet drop still evident, and (C) film coverage after drying at 350°C.

The same ink-jet printing parameters were used for depositing the TiO$_2$, ZnO, and NiO nanoparticle-laden inks in order to create a metal-oxide film between the gold
electrodes on the microhotplate platform. This is important for array development which will be discussed in Chapter 6 for utilizing multiple metal-oxide sensors for detecting more than one gas species. Optical bright field (A,C) and dark field (B,D) images were taken for NiO and ZnO nanoparticle films on the microhotplate platforms printed with the 10x10 array, and they are shown in Figure 4.15.

Figure 4.15: Bright field and dark field optical images for NiO nanoparticles (A,B) and ZnO nanoparticles (C,D) on microhotplate platforms.
For the application of studying and understanding the gas sensing properties of the metal-oxide nanoparticles on microhotplate substrates, ink-jet printing was primarily used to control the microstructure of the metal-oxide film. The microstructure and corresponding porosity of the metal-oxide film is important for allowing the analyte gases to react with adsorbed oxygen ions on the surface of the metal-oxide particles. Scanning electron microscopy was used to study the microstructure of the nanoparticle films since optical microscopy was not suitable at the size scale of interest. An SEM micrograph of the SnO₂ nanoparticle film deposited via ink-jet printing on the microhotplate substrate is shown in Figure 4.16.

![SEM micrograph of SnO₂ nanoparticles deposited via ink-jet printing on microhotplate substrate.](image)

**Figure 4.16**: SEM micrograph of SnO₂ nanoparticles deposited via ink-jet printing on microhotplate substrate.
The SnO$_2$ nanoparticles in Figure 4.16 do not show large secondary particle formation and there is little agglomeration of the particles. This is significant because agglomeration of the nanoparticle films has resulted in poor chemiresistive gas sensor performance. The most beneficial aspect of depositing the metal-oxide nanoparticles via ink-jet printing came in a comparison of metal-oxide films formed by ink-jet printing and screen printing. Figure 4.17 contains SEM micrographs for TiO$_2$ nanoparticles synthesized by the solvothermal process described previously and deposited via ink-jet printing and screen printing.

![SEM micrographs of TiO$_2$ nanoparticles deposited by ink-jet printing and screen printing for evidence of the microstructure of the metal-oxide films.](image)

**Figure 4.17:** SEM micrographs of TiO$_2$ nanoparticles deposited by ink-jet printing and screen printing for evidence of the microstructure of the metal-oxide films.
It is evident from the SEM micrographs that the TiO$_2$ nanoparticles deposited via ink-jet printing have a fairly porous microstructure, and there is not large agglomeration of the particles in the film. The screen-printed TiO$_2$ nanoparticles have the same primary particle size as the ink-jet printed film, but there is evidence in the SEM micrographs of secondary particle formation. The ink-jet printing of metal-oxide nanoparticles on microhotplate substrates is important for controlling both the location of the oxide film on the small sensor substrate and for producing a microstructure free of secondary particle formation in the film. It is also a versatile technique with the capability to deposit multiple metal-oxide nanoparticle-laden inks.

Another important property of the ink-jet printed films that was explored was the reproducibility between samples using the same printing procedure. Three separate microhotplate substrates were used and the same SnO$_2$ nanoparticle laden ink was printed on each platform with the same 10x10 array with five drops per printing location. These metal-oxide films were subsequently dried at 350°C for 3 hours and heat treated at 550°C for 4 hours. The baseline resistance of each sample in air was recorded as a function of temperature for all three samples. A plot of resistance vs. temperature is shown in Figure 4.18. At elevated temperatures (400-550°C), where chemiresistive gas sensing takes place, the baseline resistance in air for each sample has little variability. This is important for reproducibly fabricating metal-oxide sensors on microhotplate substrates by the ink-jet deposition method.
The procedure and important factors for printing nanoparticle-laden inks via ink-jet printing on microhotplate platforms has been established. Experiments were conducted in an effort to ink-jet print the SnO$_2$ microspheres by a similar method. The physical size of the SnO$_2$ microspheres (0.5-5 \( \mu \)m) posed the greatest problem for depositing the material for two main reasons. The first was a stable ink could not be formed with the SnO$_2$ microspheres because settling of the suspension occurred. This is a result of the large particle size of the material. The second challenge was during ink-jet printing of the SnO$_2$ microspheres was clogging of the orifice of the printhead causing non-uniform printing. SEM micrographs of the oxide film formation after ink-jet printing of the SnO$_2$
microspheres is shown in Figure 4.19. These micrographs depict the undesirable properties of the SnO$_2$ microspheres deposited via ink-jet printing. The SEM micrograph on the right shows a satellite drop formed from multiple drops formed instead of a singular drop. Also, there is not uniform film coverage of the material to produce a connected particle network. This is critical for the resistance measurement across the electrodes of the microhotplate sensor substrate. As a result of the difficulties of ink-jet printing the SnO$_2$ microspheres, a new deposition method was developed.

**Figure 4.19**: SEM micrographs showing the attempt of depositing SnO$_2$ microspheres via ink-jet printing.
4.3.4 Picopump Deposition System

A new deposition method was applied for depositing the larger SnO$_2$ microspheres which could not be deposited via ink-jet printing. This was done using a PV830 Pneumatic Picopump from World Precision Instruments attached to a micro-manipulator with a small glass capillary. The glass capillary had a volume of one $\mu$l and an inner diameter of 200 $\mu$m. The Picopump was attached to a compressed air cylinder and a small positive pressure was used to slowly eject particle-laden ink out of the capillary. The micro-manipulator is a device with a series of motors controlled by a joystick for accurately depositing the ink on the microhotplate platforms. A photograph of the Picopump Deposition System is shown in Figure 4.20.

Figure 4.20: Picopump Deposition System with small glass capillary and micromanipulator for location accuracy during deposition.
The SnO$_2$ microspheres were deposited using the Picopump Deposition System on silicon to determine the film formation of the particles. SEM micrographs of the SnO$_2$ microsphere film after drying at 350°C for 3 hours are shown in Figure 4.21. This deposition method maintains the nano-structure aspects of the SnO$_2$ microspheres and provides continuous film coverage which is important for gas sensor testing. This deposition method can also be used for other larger size particles which will clog the ejection orifice of the ink-jet printer.

![SEM micrographs of SnO$_2$ microspheres deposited on Si using Picopump Deposition System.](image)

**Figure 4.21**: SEM micrographs of SnO$_2$ microspheres deposited on Si using Picopump Deposition System.

### 4.4 Conclusions

Hydrothermal and solvothermal synthesis methods are useful techniques for creating nanoparticles and micron-size particles with nano-structured features for numerous
metal-oxides. The benefits of using these methods include fully crystalline nanoparticles synthesized at low temperatures with no further heat treatment required. The particle size of SnO$_2$ can also be controlled using a hydrothermal treatment by adjusting the temperature during synthesis from 4 nm to 8 nm. SnO$_2$ microspheres with nano-structured features were also created using these methods which display high surface areas despite having micron-size diameters. Nanoparticle ink formulations were made with specific rheological properties such as surface tension and viscosity corresponding to an inverse Ohnesorge number between five and seven for compatibility with the ink-jet printer.

The ink-jet printer was used to controllably and reproducibly deposit the nanoparticle-laden inks onto commercial microhotplate substrates. After drying, uniform films of metal-oxide nanoparticles were analyzed with microstructures without secondary particle formation. This is an important result that will have advantages for gas sensor testing in the two subsequent chapters. Baseline resistance measurements as a function of temperature were completed with SnO$_2$ nanoparticles deposited on micro-hotplates which display inter-device reproducibility. SnO$_2$ microspheres were unable to be deposited via ink-jet printing due to the large size of the particles which clogged the ejection orifice. A new method was developed to deposit the material utilizing a Picopump Deposition System. The accuracy of this system is not as controlled as the ink-jet printer, but it produced a consistent film of SnO$_2$ microspheres without destroying the nano-features of the particles.
Chapter 5: Comparison of Gas Sensor Performance of SnO₂ Nano-structures on Microhotplate Platforms

With the ability to create a porous microstructure of metal-oxide nanoparticle films by depositing the material via ink-jet printing on microhotplate substrates, an experimental study was conducted to determine the advantages of utilizing this microstructure compared to other particle morphologies or microstructures for the SnO₂ system. This work was inspired by the work from Kim et al. who found that hierarchical spheres of SnO₂ had increased gas sensor performance (magnitude of response and shorter response and recovery times) compared to dense agglomerated SnO₂ nanoparticles. The results of their work are shown in Figure 5.1. The investigation that was conducted was based on the premise if nanoparticles are used as the gas sensing layer and the microstructure of the oxide film is controlled to create a porous network of particles, the gas sensor results of the nanoparticles should be similar to the hierarchical particles. The tests were conducted on microhotplate platforms and dense agglomerated nanoparticles were not able to be formed as the sensing layer to reproduce their work. As a result, commercial micron-size SnO₂ particles were used to represent the dense agglomerated spheres. This chapter expands upon details and results published in Sensors and Actuators [113].
Figure 5.1: Sensor results of hierarchical SnO$_2$ spheres compared to dense agglomerated SnO$_2$ spheres for the detection of ethanol. An SEM micrograph of the microstructure of the SnO$_2$ hierarchical spheres is shown to the right. (image from Kim [78]).

The purpose of this research is to compare the gas sensor performance of SnO$_2$ nanoparticles with open microstructure (free of agglomeration) deposited via ink jet printing with nano-structured microspheres (hierarchical particles) and micron-size particles on microhotplate platforms. The effect of particle size and the influence of the microstructure of the oxide-film on the response and transient effects of the sensor are presented. A brief summary of the gas sensor principles in Chapter 2 and ink-jet printing advantages presented in Chapter 4 are given in the subsequent introduction.
5.1 Introduction

A drive towards miniaturized gas sensor platforms in the form of microhotplates, or MEMS devices has garnered increased attention for metal-oxide sensors [13, 19, 30, 84, 143, 144]. The benefits of using microhotplate platforms include increased portability and reduced power consumption compared to traditional thick-film metal-oxide sensors on alumina substrates. In addition to the development of microhotplate platforms for miniaturized metal-oxide sensors, synthesizing oxide nano-structures with a specific morphology has led to increased gas sensor performance [62, 145-148]. These nano-structures consist of a hierarchical structure with small clusters or sheets of particles connecting to form a micron-size particle with enhanced surface area compared to spherical particles. These nano-structures have been termed hierarchical nano-sheets [149], nano-structured microspheres [150], nano-flowers [151], and nano-urchins [152] as well as other descriptions in literature [153-155].

These nano-structures benefit from having a large surface-to-volume ratio and a sensing layer consisting of a porous network of particles which allows quick access of the gas through the film [62, 148]. Nanoparticles also display a high surface area and have been a focus of gas sensor research [5, 7, 36]. When nanoparticles are deposited and consolidate into a film, aggregation between the nanoparticles becomes very strong since van der Waals attraction is inversely proportional to the particle size [156, 157]. Nanoparticles prefer to combine and form large agglomerates which can serve as secondary particles [5]. Large agglomerates of nanoparticles have shown to negatively
influence sensor performance through decreased sensitivity and longer recovery times [62, 145, 147].

These nanoparticle films which are heavily agglomerated were printed using thick-film techniques on alumina sensor substrates. Thick-film printing is not applicable for microhotplate platforms due to the small size of the device, and it is difficult to control the microstructure of the nanoparticle-film using this method. In the previous chapter, it was shown that nanoparticle films with an open microstructure free of agglomeration can be formed on microhotplate substrates using an ink-jet printer [158]. The microstructure of the nanoparticle-film created by ink-jet printing maintains a large surface area similar to the nano-structured microsphere film. However, gas sensor experiments on miniaturized sensor substrates comparing non-agglomerated nanoparticles and nano-structured microspheres have not been thoroughly conducted until now.

5.2 Microhotplate Gas Sensor Testing Facility

A small stainless steel cube generally used in ultra high vacuum (UHV) technology was used as the gas sensing chamber for the gas sensor measurements. The microhotplate devices with the metal-oxide films are placed inside the gas sensing chamber and are press-fitted into two pin connectors. These connectors are wired to terminal blocks and feed-through flanges are used to wire the devices from the gas sensing chamber to the Keithley sourcemeters. A photograph of the micro-hotplates inside the gas-sensing chamber is shown in Figure 5.2. Two microhotplates are able to be tested simultaneously which is important for reproducibility experiments.
Figure 5.2: Two microhotplate sensor substrates plugged into gas sensing chamber for testing to analyze gas concentrations.

Gas sensor experiments were performed using a custom microhotplate testing facility. Samples were placed within a stainless steel chamber connected to two dual-channel Keithley sourcemeters for testing multiple samples at one time. Gas flow to the sample chamber was regulated through the use of MKS mass flow controllers (MFCs). A photograph of the MFCs with a gas mixer and the sample chamber is shown in Figure 5.3.
Figure 5.3: Photograph of mass flow controllers, gas mixer, and gas sensing chamber. These are components of the microhotplate testing facility.

A Keithley 2602A dual-channel sourcemeter was used to control the microhotplate temperature while a Keithley 2636A dual-channel sourcemeter was used for recording the sample resistance. The microhotplate temperature was controlled by supplying a voltage to the platinum heater of the microhotplate. A more detailed explanation
supplied by the manufacturer is located in Appendix B. Resistance measurements were registered every three seconds during gas sensor testing. LabVIEW software was used to automate the system and log measurements during gas sensor testing. A total flow rate of 1 L/min was sustained at all times, and tests were conducted in a background of dry air. Methane and carbon monoxide were supplied at specific concentration levels during testing. Methane ranged from 0.05-1% while CO ranged from 10-100 ppm. The nitrogen and oxygen flow rates were adjusted to maintain a constant ratio of oxygen to nitrogen to ensure a background of dry air throughout the test. A more detailed explanation of the oxygen concentration maintained as part of the gas sensing tests is provided in Appendix C. Response values for the gas sensor measurements were calculated using an average of three addition and removal cycles of the analyte gas during testing.

5.3 SnO$_2$ Nano-structures and Microstructure Formation

SnO$_2$ nanoparticles and microspheres were synthesized using hydrothermal methods in order to control particle size and morphology. The SnO$_2$ micron-size were purchased from Sigma Aldrich and they were designated as -325 mesh. The experimental procedure for the synthesis of SnO$_2$ nanoparticles and microspheres was explained in Chapter 4.2.1 and 4.2.2. An x-ray diffraction scan was conducted on the SnO$_2$ nanoparticles, microspheres, and micron-size particles, with a plot of this data shown in Figure 5.4.
All samples displayed peak intensities consistent with the cassiterite phase of SnO\textsubscript{2}. Differences in relative peak broadness are evident in the plot with SnO\textsubscript{2} nanoparticles having the broadest peaks followed by microspheres and micron-size particles. SnO\textsubscript{2} microspheres and micron-size particles displayed a similar overall size. However, the microspheres were assembled from plate-like two dimensional nano-structures which explain the slightly broader peaks of these structures compared to the micron-size particles.
The particle size of the SnO$_2$ nanoparticles was calculated using the Debye-Scherrer equation to be 9 nm. The Brunauer, Emmett, and Teller (BET) measurements determined a surface area of 97 m$^2$/g for the SnO$_2$ nanoparticles. This surface area is in agreement with the particle size calculated using the Debye-Scherrer equation for spherical particles. The surface area of the SnO$_2$ microspheres was found to be 54.3 m$^2$/g utilizing BET measurements which can be explained by the nano-structured features protruding from the center of the particle.

The SnO$_2$ nanoparticles were deposited on the microhotplate substrate via ink-jet printing as described in Chapter 4.3.3. Briefly, a 10x10 array of the SnO$_2$ nanoparticle ink was deposited with a spacing of 20 μm and 5 drops deposited per printing location. The metal-oxide film was dried at 350°C for 3 hours and heat treated at 600°C for 4 hours. Optical images and SEM micrographs of the SnO$_2$ nanoparticle sample are shown in Figure 5.5. As described previously, the SnO$_2$ microspheres and SnO$_2$ micron size particles were not able to be deposited via ink-jet printing so the Picopump Deposition System was used to create the metal-oxide films for these samples. Optical images of the dried film formation of the SnO$_2$ micron-size particles and SnO$_2$ microspheres are shown in (A) and (B) of Figure 5.6, respectively. The accuracy of the films deposited by the Picopump Deposition System is not as accurate as the ink-jet printing system. However, there was sufficient coverage between the electrodes on the microhotplate platform to conduct gas sensor measurements.
Figure 5.5: Optical images and SEM micrographs of SnO$_2$ nanoparticle film deposited via ink-jet printing on the microhotplate sensor platform.

Figure 5.6: Optical images of dried metal-oxide films on microhotplate platforms for (A) SnO$_2$ micron-size particles and (B) SnO$_2$ microspheres.
The microstructure of the three metal-oxide samples was analyzed using SEM. Figure 5.7 contains two micrographs for the SnO₂ nanoparticles film deposited via ink-jet printing. The oxide-film in Figure 5.7 (b) displays an open microstructure with little agglomeration. SEM micrographs of both the microspheres and micron-size particle films can be seen in Figure 5.8. The film microstructures were found to be uniform, although the micron-size particles were found to be in the sub-micron range. The −325 mesh designation for the micron-size SnO₂ particles certifies that the particle size is less than 44 microns. From the SEM micrograph in Figure 5.8 (a), the particles are much smaller than this designation; however, they are much larger than the SnO₂ nanoparticles in Figure 5.7(b).

Figure 5.7: SEM micrograph of SnO₂ nanoparticles (a) coverage on microhotplate and (b) microstructure of oxide film.
Figure 5.8: SEM micrograph displaying microstructure of SnO$_2$ films for (a) micron-size particles and (b) microspheres.

5.4 Gas Sensor Performance

The SnO$_2$ nanoparticles, microspheres, and micron-size particles were tested for sensing methane and carbon monoxide in a background of dry air to compare the response and transient properties (response and recovery times) of these materials on microhotplate platforms. Response, or sensitivity, of the sensor can be defined differently; for this research article, it is defined as the ratio of the baseline resistance in air ($R_a$) to the resistance when the analyte gas is in the system ($R_g$). Therefore, the response is calculated as ($R_a/R_g$).

A plot of the resistance vs. time for SnO$_2$ nanoparticles on a microhotplate sensor substrate to 35 ppm CO in background of dry air is shown in Figure 5.9. The decreased
resistance in response to the addition of CO is consistent with an n-type semiconductor. The baseline resistance of the metal-oxide film decreased with increasing temperature. The sensor response was found to peak at 500°C and decreased with further temperature elevation. However, 90% response (τ90%-response) and recovery times (τ90%-recovery) were faster at higher temperatures. This is shown by the more rapid leveling off of the resistance values.

Figure 5.9: Plot of resistance vs. time for SnO2 nanoparticle film on microhotplate sensor substrate to 35 ppm CO in a background of dry air.

Sensor response to a fixed CO concentration of 35 ppm as a function of temperature was performed on all three SnO2 particle types, with results shown in Figure 5.10. The
SnO₂ nanoparticle sample deposited by ink-jet printing is designated as the blue dotted line with the diamond markers. The SnO₂ microsphere is distinguished by the red dashed line with circle markers and the SnO₂ micron-size particles are shown as the black dotted line with triangle markers. This notation is consistent throughout the rest of the chapter. This sensing test was conducted to determine the temperature at which maximum sensor response was achieved. The sensor response was a maximum at 500°C for both the microsphere and nanoparticle films, and was near maximum at this temperature as well for the micron-size sample.

Figure 5.10: Plot of response as a function of temperature for SnO₂ films on microhotplate devices when exposed to 35 ppm CO.
The nanoparticles displayed a higher response than the microspheres and a much larger response than the micron-size particles. This is in contrast to reports that microspheres display much higher response than heavily agglomerated nanoparticles in literature [145]. The foremost difference between the experiments is the microstructure of the nanoparticle films. Utilizing the ink-jet printer, an open microstructure without heavy agglomeration was produced which aids in the gas sensing performance of the SnO$_2$ nanoparticles to CO. Both the nanoparticles and microspheres, displayed much higher response to CO than the micron-size particles despite the micron-size particles having a similar open microstructure. This occurred due to the higher surface area of the nanoparticles and microspheres compared to the micron-size particles. It is important to note that the surface area of the metal-oxide as well as the microstructure of the metal-oxide film contribute to sensor performance. In addition to a higher surface area achieved through the use of nanoparticles, the particle size is close to twice the Debye length for SnO$_2$ which has been shown to result in fully depleted grains. Upon the addition of the analyte gas, a change in the bulk carrier concentration can improve sensing performance.

Gas sensor tests to a range of CO levels were performed at the temperature with the highest response given in Figure 5.10. A plot of the response vs. CO concentration for the three materials is shown in Figure 5.11.
Figure 5.11: Plot of response vs. CO concentration at a fixed temperature for SnO$_2$ films.

A positive correlation between the response and increasing CO concentration was deduced from the plot. The response began to level off as the sensors were exposed to higher concentrations. Ninety percent response ($\tau_{90\%-\text{response}}$) and recovery times ($\tau_{90\%-\text{recovery}}$) for the three SnO$_2$ materials were calculated when exposed to 35 ppm CO at 500°C. The results are shown in Table 5.1.
Table 5.1: 90% response ($\tau_{90\%-response}$) and recovery times ($\tau_{90\%-recovery}$) of SnO$_2$ particles to 35 ppm CO at 500°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Response time (sec)</th>
<th>Recovery time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoparticles</td>
<td>18</td>
<td>151</td>
</tr>
<tr>
<td>Microspheres</td>
<td>14</td>
<td>125</td>
</tr>
<tr>
<td>Micron-size</td>
<td>41</td>
<td>102</td>
</tr>
</tbody>
</table>

The response times for the nanoparticles and microspheres were short (<20 seconds), while the micron-size particles had over twice the response time at 41 seconds. The quicker response times for the nanoparticles and microspheres may be due to the higher surface area of the materials and reaction of CO with the adsorbed oxygen species on the surface of these materials. The recovery times for all three structures were on the order of 2-3 minutes. While this is not a rapid recovery time for the nanoparticles and microspheres, the open microstructure of the SnO$_2$ films allows the analyte gas to diffuse in and out of the film fairly quick. The micron-size particles had the shortest recovery time of the three materials even though it displayed the longest response time. This is an unexpected result since the porosity of the SnO$_2$ films should be similar.

In addition to gas sensor experiments to CO, response to a fixed 0.4% methane concentration as a function of temperature for the nanoparticle, microsphere, and micron-
size particles is shown in Figure 5.12. The SnO$_2$ microspheres displayed the highest response at 550°C for all three materials with the highest response by the nanoparticles at 500°C and the micron-size particles at 600°C. Even though the SnO$_2$ microspheres displayed the highest sensitivity at 550°C, the resistance of the material began to drift significantly at this temperature. At 600°C, the SnO$_2$ microspheres did not have a stable baseline resistance and an average response value was not plotted at this temperature. For these reasons a fixed temperature test was performed for the SnO$_2$ microspheres at 500°C.

![Figure 5.12](image_url): Plot of response as a function of temperature for SnO$_2$ films on microhotplate devices when exposed to 0.4% CH$_4$. 

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The sensors were then exposed to increasing methane concentration levels. Response values are plotted in Figure 5.13. The response increased with rising methane concentration for all three SnO$_2$ particles. The microspheres displayed higher response values to methane than the nanoparticles, but the opposite was true when the metal-oxide films on microhotplate platforms were exposed to CO. This may be a result of the difference in surface chemistry of the SnO$_2$ nanoparticles and microspheres since they were synthesized using different precursors. However, both the microspheres and nanoparticles displayed much higher sensitivity to methane and CO compared to the micron-size particles.

Figure 5.13: Plot of response vs. CH$_4$ concentration at a fixed temperature for SnO$_2$ films.
5.5 Conclusions

The gas sensor performance comparison between SnO$_2$ nanoparticles with open microstructure (free of agglomeration) deposited via ink jet printing, nano-structured microspheres and micron-size particles on microhotplate platforms provided important conclusions for the development of nano-structured oxide films for detecting methane and carbon monoxide for coal mining applications. The SnO$_2$ nanoparticles had gas sensor response similar to or better than the SnO$_2$ microspheres to the analyte gases. Both materials greatly outperformed the SnO$_2$ micron-size particles. This is important because the small particle size and corresponding high surface area for the nano-structured materials led to more reaction of the reducing gases with adsorbed oxygen ions on the surface of the material.

In addition to the particle size, the microstructure of the metal-oxide film was found to be critical to the device performance. In the study by Kim et al., the SnO$_2$ microspheres had much higher gas sensor response compared to agglomerated dense SnO$_2$ nanoparticles. However, the result of this investigation found that by controlling the deposition of the metal-oxide nanoparticulate film through ink-jet printing, the corresponding microstructure of the film was free of agglomeration and porous. As a result, the gas sensor response for the SnO$_2$ nanoparticles and microspheres were similar to specific concentrations of methane and carbon monoxide.

This is a very important conclusion for the array development of gas sensor research which involves incorporating other metal-oxide materials in addition to SnO$_2$. In Chapter 4, methods for synthesizing and depositing TiO$_2$, ZnO, and NiO nanoparticles with an
open microstructure via ink-jet printing were described. Using multiple metal-oxide materials is beneficial for overcoming issues of cross-sensitivity which plague chemiresistive metal-oxide sensors. The study in this chapter was beneficial to develop highly sensitive devices utilizing metal-oxide nanoparticles without having to use metal-oxide hierarchical particles or microspheres with more sophisticated geometries. In addition, the reproducibility of depositing nanoparticle-laden inks via ink-jet printing is crucial for commercial applications.
Chapter 6: Development of Nanoparticle Array for Detecting Methane and Carbon Monoxide

In the preceding chapters, the importance of particle size and microstructure of the metal-oxide sensing film for chemiresistive sensors has been described extensively. Chapter 4 explains the methodology for depositing the metal-oxide nanoparticles with a porous microstructure via ink-jet printing in a controllable and reproducible manner on the miniaturized gas sensing platforms. Chapter 5 indicates that the use of SnO$_2$ nanoparticles deposited by this method displayed high-quality gas sensor response to concentrations of carbon monoxide and methane critical for coal mining applications. Gas sensor testing in the previous chapter was done in a background of dry air to the analyte gases separately. However, the application of interest involves detecting concentrations of both carbon monoxide and methane in the environment simultaneously.

Both analyte gases are reducing by nature which causes the resistance of n-type semiconductors (SnO$_2$, TiO$_2$, and ZnO) to decrease when either or both gases are present. This decrease in resistance or increase in conductance has been described in Chapter 2 due to the reaction with adsorbed oxygen ions at the surface, and a corresponding donation of electrons available for conduction. The rate of this reaction and the ensuing change in resistance of the metal-oxide film depends on the material, operating temperature, microstructure of the metal-oxide film, and concentrations of both carbon
monoxide and methane. Ideally, one of the metal-oxides would show gas sensor response to one of the gases at a specific temperature, but the resistance would not change in the presence of the other analyte gas. This is defined as having a sensor element which is selective to a specific gas. However, chemiresistive metal-oxide sensors are notoriously cross-sensitive to many reducing or oxidizing gases which dictates that they are not selective to one gas or the other. For this reason, the use of multiple metal-oxides to form an array of sensors on one device is beneficial for detecting each gas at the concentrations of interest.

This following experimental study was conducted to develop an array of sensor elements using four metal-oxide nanoparticles deposited via ink-jet printing on microhotplate substrates to simultaneously detect methane and carbon monoxide for coal mining applications. A design of experiments was conducted to determine the operating temperature which provided the most disparity for both gases for each material. Principal component analysis (PCA) was used to accomplish this by identifying the covariance between the two gases at each temperature. A linear-based model was developed for prediction of methane and carbon monoxide concentrations in the presence of one another for the array. This model was tested for validation to a new series of gas concentrations.

6.1 Introduction

Chemiresistive sensor array devices have been used for numerous applications for the last 30 years to overcome the inherent problems with cross-sensitivity for the metal-oxide
films [159]. This includes, but is not limited to, applications in detecting body odor [18], bacteria such as *E. coli* and *Salmonella Typhimurium* [160], organic vapors such as toluene and benzene [161], alcoholic vapors [162], defense monitoring [144], food spoilage [163], and non-invasive medical diagnostics [19]. The implementation of gas sensor arrays for developing selective sensors in complex environments is sometimes defined as electronic nose technology. The build-up of multiple sensor elements mimics the human olfactory system which “senses” gases or smells in complex backgrounds.

In order to create a gas sensor array capable of detecting multiple gases simultaneously, a series of gas sensor tests and analysis of the results were performed. This introduction will serve to define the three methods used for the development of the array; they are the creation of a design of experiments, selection of an optimum operating temperature using principal component analysis, and construction of a predictive model and corresponding validation testing. In order to understand the effect of multiple variables (i.e. operating temperature, CO concentration, and CH₄ concentration), a design of experiments was constructed to determine the interaction of these variables. Design of experiments (DOE) is an effective method to apply a systematic approach to test all factors simultaneously. This eliminates a trial-by-error method of experimental testing by changing one factor at a time while holding all other variables constant. The one factor at a time method is not conducive for providing information on the interaction of temperature, carbon monoxide concentration and methane concentration for our system.

There are a few important principles in the set-up of a DOE which is beneficial for obtaining accurate experimental data. In the construction of a DOE, independent
variables need to be clearly defined and the specific level of each variable needs to be determined [164]. The more levels of each variable will result in a larger number of states to be tested with can lead to lengthy experiments. This involves the development of a variable matrix where the factors are defined and a corresponding design matrix with the testing parameters. In addition to the construction of the design matrix, randomization of the states is critical to remove any bias or hysteresis that can occur during testing. Replication of the design matrix is also beneficial for better statistical analysis. There is a distinct difference between replication of an experiment and repetition of experiments which should be characterized. Repetition in an experiment involves testing to a specific state in succession while replication involves repeating the design matrix. Replication is beneficial to help identify sources of variation, to understand the interaction of the variables, and to further strengthen the reliability of the results.

The DOE will generate a large amount of data which is difficult to analyze due to the number of variables and interaction between the variables. Principal component analysis (PCA) is one statistical tool used as a means of identifying pattern in data, and expressing that data in such a way to analyze their similarities and differences. In tests with more than two variables (i.e. higher dimensions), patterns in the data can be hard to identify due to graphical representations in higher dimensions difficult to understand and analyze. The main advantage of PCA is to determine patterns in data of higher dimensions by compressing the data and reducing the number of dimensions, without much loss of information.
There are several books and research articles which detail PCA in general, and these should be referred to for an in-depth discussion of this method [165-167]. A brief description of the technique is necessary for subsequent sections in this chapter. For this study, the difference in resistance of the metal-oxide film from the baseline condition in air to a new value in the presence of carbon monoxide, methane, or both gases is critical for detecting the concentration of the analyte gases. This distance or “spread” from the mean of the data set is defined as the variance. The variance for a variable, X, over n number of samples is shown in equation 6.1 with the sample mean defined by \( \bar{X} \). The variance can be used for data sets which are 1-dimensional, but for the application of interest, there are multiple dimensions. For this reason, the covariance of the data set is utilized to determine the differences in the data set between dimensions. The covariance measures the strength of the linear relationship between two variables through the mean of the product of the deviations from the dimensional mean [168]. The covariance is always measured between 2-dimensions, but a covariance matrix can be calculated for higher dimension tests. The covariance is shown in equation 6.2 and the covariance matrix for 3-dimensions (x,y, and z) is defined in equation 6.3.

\[
\text{var}(X) = \frac{\sum_{i=1}^{n} (X_i - \bar{X})(X_i - \bar{X})}{n - 1} \quad (6.1)
\]

\[
\text{cov}(X, Y) = \frac{\sum_{i=1}^{n} (X_i - \bar{X})(Y_i - \bar{Y})}{n - 1} \quad (6.2)
\]
Principal component analysis uses the covariance matrix to represent the variability between the states of testing in the design of experiments. After the covariance matrix is calculated, eigenvalues and eigenvectors are calculated from the covariance matrix which must be square. The eigenvector with the highest eigenvalue is defined as the principal component of this data set and conveys the most significant relationship between the data dimensions. The two largest eigenvalues and corresponding eigenvectors are taken as the principal components of the data set. The data from the multidimensional data set can now be graphically represented in 2-dimensions by the principal components calculated from the covariance matrix. The purpose of PCA is to express the main information in the variables (X) by a lower number of variables which are the principal components of X [164]. Principal component analysis has been used to understand interaction effects on sensors including surface acoustic wave (SAW) sensors [169] and metal-oxides for an aroma study for custard detection [170]. A few detailed experimental studies are presented to show the benefits of using PCA.

A study by Chen et al. involved vertically aligned ZnO nanorod arrays coated with SnO$_2$/noble metal nanoparticles for selective gas detection [171]. They constructed an array of three oxide sensors with different coatings to detect multiple gases including NO$_2$, H$_2$S, NH$_3$, H$_2$, and CO. The gas sensor response strengths (sensitivity) of each sample were used to determine if the response strength could be used to differentiate between the numerous gases. Their PCA graph is shown in Figure 6.1. From the graph,
the data points could be grouped in clusters, and most of the clusters were well separated, which indicates the sensor array is strongly selective.

![PCA analysis of sensing responses of the sensor array. The data results are clustered by gas type (image from Chen [171]).](image)

**Figure 6.1:** PCA analysis of sensing responses of the sensor array. The data results are clustered by gas type (image from Chen [171]).

In addition to the work by Chen et al., a research study by Ivanov was conducted for detection of volatile organic compounds at multiple gas concentrations using metal-oxide chemiresistive sensors [144]. This work involved operating WO\textsubscript{3} sensors at different temperatures in the presence of singular and multiple analyte gases. This work most resembles the analysis that was performed by the author in the later sections. The PCA graph for the study by Ivanov is shown in Figure 6.2.
Figure 6.2: Results of PCA using the responses of a 4-element WO$_3$ sputtered microsensor array (graph from Ivanov [144]).

From the plot in Figure 6.2, the data points display clustering to the specific gas concentrations and combinations of gases. In the plot, C1, C2, and C3 designate certain levels of the gas concentration. The description of principal component analysis and the corresponding examples were presented to provide the reader the benefits of using pattern recognition techniques to analyze multidimensional data effectively.

The ultimate goal is to develop a gas sensor array to selectively detect methane and carbon monoxide gas concentrations simultaneously in the presence of one another. In
order to accomplish this, a DOE was created and PCA was performed to understand the relationship between material, operating temperature, and each gas concentration. Based on the DOE conducted to optimize the operating temperature, the next objective is to monitor the resistance of the metal-oxide film to predict values for the concentrations of methane and carbon monoxide. The DOE can be used as calibration data to produce a predictive model through a calibration method [164]. Predictive modeling can be developed in a forward sense in order to predict the gas concentration as a function of metal-oxide film resistance. This type of calibration has been in common use for many years in chemical analysis, and there are well-defined cases where it can be valuable [164, 172, 173]. After a predictive model is created, validation experiments must be performed to test the reliability and accuracy of the predictive model.

One example of the construction of a predictive model using metal-oxide sensors and the corresponding validation testing was performed by Siripatrawan [160]. This study involved using an oxide array in the form of an electronic nose to detect gases associated with E. coli and S. Typhimurium cultures. Both n-type and p-type metal-oxide sensors were used in the electronic nose for good variability between the sensor elements. A plot of predicted concentration vs. true concentration of the bacteria strains is shown in Figure 6.3. From this plot, it can be discerned that the predicted model shows good accuracy when tested to several concentrations of bacteria strains. The $R^2$ value of 0.96 is close to one which determines the linearity of the validation testing.
6.2 Design of Experiments for Temperature Determination

A DOE was constructed and tested for understanding the relationship between the four main variables for the chemiresistive gas sensor array device for coal mining safety. Analysis was performed by PCA after testing in order to graphically illustrate the
covariance between the variables and determine the temperature with the most difference for each material for carbon monoxide and methane detection. The construction of a 4 element array using the multiple metal-oxide nanoparticles at specific operating temperatures is described. The data for SnO$_2$ and NiO will be presented in this dissertation while the data for TiO$_2$ and ZnO will be stated, but not shown. This is done for clarity and to reduce confusion in the document due to the large amount of data generated by the DOE and subsequent analysis.

6.2.1 Design of Experiments

For the application of interest for this dissertation, a variable matrix was constructed in order to identify the four main variables that would affect the resistance of the metal-oxide film during gas sensor testing. The variables are the metal-oxide nanoparticles (SnO$_2$, ZnO, TiO$_2$, and NiO), the operating temperature of the sensor, the carbon monoxide concentration, and the methane concentration. The variable matrix is shown in Table 6.1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>SnO$_2$, ZnO, TiO$_2$, NiO</td>
</tr>
<tr>
<td>Temperature</td>
<td>350 - 600°C</td>
</tr>
<tr>
<td>CO concentration</td>
<td>0 – 100 ppm</td>
</tr>
<tr>
<td>CH$_4$ concentration</td>
<td>0 – 1 %</td>
</tr>
</tbody>
</table>

Table 6.1: Variable matrix for design of experiments for detecting CO and CH$_4$ concentrations at a range of temperatures for four metal-oxides.
The range for each variable is also given in the variable matrix. The importance of the operating temperature was defined in Chapter 2 with the temperature affecting the species of adsorbed oxygen ions on the surface of the material and shown in practice in Chapter 5 for SnO\textsubscript{2} nanoparticles displaying gas sensor response as a function of operating temperature. The carbon monoxide and methane concentration ranges were described previously in coal mining applications for toxicity and explosion prevention, respectively.

The variable matrix in Table 6.1 identifies the variables which will be explored in the DOE, but it is important to note that many other factors were held constant for this experimental study. The metal-oxide nanoparticles were synthesized using the appropriate hydrothermal or solvothermal method illustrated in Chapter 4. They were formulated into an oxide-laden ink and deposited on the microhotplate substrates via ink-jet printing with the following parameters: a 10x10 array with 20 micron spacing and 5 drops per trigger location. The microhotplate sensors were dried and heat-treated at 600°C to prevent any changes to the film microstructure during testing.

The four independent variables were defined in the variable matrix in Table 6.1 and the measured dependent variable is the resistance of the metal-oxide film at the operating temperature in an environment of carbon monoxide, methane, or both gases. This metal-oxide film resistance can be converted to a gas sensor response through the equation:

\[ S = \frac{R_{\text{air}}}{R_{\text{gas}}} \]

This variable matrix was transformed into a design matrix for actual gas
sensor testing. There were three levels of testing for the temperature, CO concentrations, and CH₄ concentrations. The metal-oxide material is discrete and cannot be varied. Each metal-oxide material was tested to the design matrix. The design matrix for the SnO₂ nanoparticle sensor is shown in Table 6.2.

<table>
<thead>
<tr>
<th>Level</th>
<th>Temperature</th>
<th>CO concentration</th>
<th>CH₄ concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>450</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>500</td>
<td>35 ppm</td>
<td>0.5%</td>
</tr>
<tr>
<td>2</td>
<td>550</td>
<td>100 ppm</td>
<td>1%</td>
</tr>
</tbody>
</table>

Table 6.2: Design matrix for design of experiments test for SnO₂ nanoparticle sensor.

The CO and CH₄ concentrations were used at these three levels for all the metal-oxide materials. The temperature range was varied for certain metal-oxides (500-600°C for TiO₂, 400-500°C for NiO, and 450-550°C for ZnO) due to prior knowledge of the appropriate temperature regions for these materials. All levels were tested for each of the metal-oxide materials which resulted in 27 total states for testing. The 27 states were randomized to eliminate any hysteresis and/or bias during testing. The transformation from the design matrix to the order of testing is shown in Table 6.3. The DOE test in Table 6.3 was replicated three times in order for better statistical analysis of the results.
Table 6.3: Randomization of design of experiments to show the order each state was tested in order to prevent bias and/or hysteresis.

Each state consisted of testing to a specific temperature, CO concentration, and CH₄ concentration for each material. In order to calculate the gas sensor response ($R_a/R_g$) for each state, the baseline resistance at the operating temperature must be known. For this reason, the metal-oxide sensor was held at the operating temperature for ten minutes prior to the testing to a “state”. The analyte gas levels were introduced for 3 minutes and then returned to a background of dry air. The raw data gas sensing results for the SnO₂ microhotplate sensor subjected to the DOE is shown in Figure 6.4.
Figure 6.4: Raw gas sensing data for SnO$_2$ nanoparticles tested at 3 different temperatures with combinations of CO and CH$_4$ gas concentrations. (A) This plot displays the full test and (B) shows a portion of the test with response to each state indicated by the red asterisk.
From the plot in Figure 6.4 (A), it is shown that the DOE results in a large amount of data which must be analyzed to provide information and understanding on the interaction of the variables. The plot in Figure 6.4 (B) is more beneficial to actually visualize the decrease in resistance of the SnO$_2$ nanoparticle film during a state indicated by the red asterisk. Each state has a specific concentration of analyte gas provided in the DOE. The gas sensor test takes place over a long amount of time (~18 hours). A portion of the DOE conducted for the NiO nanoparticles on a microhotplate sensor platform is shown in Figure 6.5.

![Graph](image)

**Figure 6.5:** Raw data for gas sensor testing of NiO nanoparticles tested to design of experiments. Red asterisks indicate a state where CO, CH$_4$, or both gases are introduced and removed from the system.
While the TiO₂ and ZnO raw data plots to the DOE are not shown, both materials display n-type semiconductor properties (decrease in resistance to the reducing gases). A portion of the raw data plot for the NiO DOE test is shown in Figure 6.5, and this material shows p-type response (increase in resistance to the reducing gases). Having a p-type material in the sensor array is important for the pattern recognition aspects described in the subsequent sections.

The DOE tests to each material provided a large amount of data which will be displayed in a few ways to understand the interaction between the operating temperature, carbon monoxide, and methane gas concentrations. The first way it will be presented is graphically as gas sensor response as a function of methane at a specific operating temperature in a background of carbon monoxide gas. This is shown for the SnO₂ sample in Figure 6.6 (A). This graph shows that the gas sensor response for the SnO₂ nanoparticles is highly dependent on the methane concentration and operating temperature of the sensor. The lines in the graph of the same color are grouped by operating temperature, and the different background concentrations of gas (0, 35, and 100 ppm CO) are designated by different markers and dotted/dashed lines. The carbon monoxide concentration does not provide a significant contribution to the gas sensor response. The same data was plotted for the SnO₂ gas sensor response as a function of carbon monoxide concentration and is illustrated in Figure 6.6 (B). The horizontal lines in the plot confirm the point that for the SnO₂ sample, the carbon monoxide concentration does not contribute very much to the gas sensor response.
Figure 6.6: Gas sensor response as a function of (A) methane concentration and (B) carbon monoxide concentration at 3 different temperatures in various backgrounds for the SnO$_2$ nanoparticle sensor.
Similar analysis was performed for the other metal-oxide materials to gain some understanding of the relationship between the variables. The results of these plots are shown for NiO in Figure 6.7 (A) and (B). The gas sensor response in these graphs is at a value between 0 and 1 due to the p-type semiconductor behavior of the NiO material and the way the gas sensor response is defined. The important information from these plots for the NiO nanoparticles is that the gas sensor response depends on both the methane and carbon monoxide gas concentration, in addition to operating temperature of the oxide film.

The nickel oxide material is generally more favorable for carbon monoxide detection than methane detection due to the inherent electronic properties of the material and reaction with the adsorbed oxygen ions on the surface of the oxide. However, the concentration of methane for this application is much larger than that for carbon monoxide detection. The detection limit for methane is one percent which is equivalent to 10,000 ppm CH\(_4\) while the detection limit for carbon monoxide is 100 ppm. The application is to detect methane and carbon monoxide simultaneously even though the CH\(_4\) concentration is 100x larger than the CO concentration.
Figure 6.7: Gas sensor response as a function of (A) methane concentration and (B) carbon monoxide concentration at 3 different temperatures in various backgrounds for the NiO nanoparticle sensor.
The DOE was beneficial in generating a large amount of data which was used to understand some of the relationships between operating temperature, carbon monoxide concentration, and methane concentration for each of the four metal-oxide materials. However, the multidimensional variables make it difficult to understand the effect of which operating temperature gives the most variance between the methane and carbon monoxide gas concentrations. This temperature is important to designate for the array elements in order to predict the analyte gas concentrations using only the resistances of the metal-oxide sensors.

6.2.2 Principal Component Analysis

The data generated by the DOE was analyzed using PCA to select the operating temperatures for each metal-oxide. This was completed by using Matlab software in order to calculate the covariance matrix and corresponding eigenvalues and eigenvectors which will be designated as the principal components of the data set. The fundamental methodology for using PCA was described in the introduction. The covariance matrix was constructed using three variables for each material. The two independent variables were the CO and CH₄ concentration, and the dependent variable was the resistance of the metal-oxide film. The resistance of the metal-oxide film was converted to gas sensor response which gives a more useful physical description of the dependent variable. The data was preprocessed to be mean-centered in which the mean was subtracted from each data point for each variable.

The three variables were used to construct a 3x3 covariance matrix which gives information on the strength of the linear relationship between the gas sensor response and
each analyte gas concentration. Data for all three operating temperatures of the metal-
oxide films were used to calculate the covariance. The principal components which were
the largest eigenvalues of the covariance matrix were used to graphically represent the
data of higher dimensionality. The PCA results for the SnO$_2$ nanoparticle sample is
shown in Figure 6.8.

![Figure 6.8: PCA analysis for SnO$_2$ nanoparticle sensor. Clustering of the data shows the impact of operating temperature, CO concentration, and CH$_4$ concentration on gas sensor response.](image-url)
The graph in Figure 6.8 has a lot of information which is useful to understand the interaction of the variables studied in the DOE. The blue diamonds in the graph are the data points which correspond to a gas sensor response value calculated at a specific operating temperature, carbon monoxide gas concentration, and methane gas concentration. The PCA allows for grouping or clustering of the data with similar resistances or gas sensor responses. The red circles in Figure 6.8 were drawn after testing to highlight the clustering of the results which are heavily dominated by temperature and methane concentration for the SnO$_2$ sample.

The top right data points in Figure 6.8 are the gas sensor response to air and carbon monoxide concentrations at multiple temperatures without methane present in the environment. There is not much differentiation between the data points in this region which confirms the results in Figure 6.6 that the SnO$_2$ nanoparticles cannot be used to predict carbon monoxide concentrations at these specific operating temperatures. However, there is clustering of the gas sensor responses to specific methane concentrations as a function of operating temperature which is important for determining a suitable temperature for this array element. The operating temperature selected for the SnO$_2$ sample after PCA, was 500°C due to the tight clustering of these data points and high values of gas sensor response. Even though 550°C has a higher gas sensor response for the SnO$_2$ nanoparticles shown in Figure 6.6, PCA depicted in Figure 6.8 determined that operating the sensor at 500°C would be beneficial for accurately detecting methane in the presence of carbon monoxide. It is important to point out that PCA should not be
used without some physical understanding of the data set because it is a linear unsupervised method of data reduction.

Principal component analysis was also performed for the other three metal-oxide nanoparticles subjected to the DOE. To this point NiO has been presented in conjunction with SnO$_2$. However, for PCA it is more beneficial to show the ZnO data set since both SnO$_2$ and ZnO are n-type semiconductors. The comparisons between the n-type semiconductors will be more visually beneficial. The PCA graph for the ZnO nanoparticles subjected to the DOE is shown in Figure 6.9.

![PCA graph for ZnO nanoparticle sensor](image)

**Figure 6.9:** PCA analysis for ZnO nanoparticle sensor. Clustering of the data shows the impact of operating temperature, CO concentration, and CH$_4$ concentration on gas sensor response.
There are some similarities and differences in the ZnO PCA plot compared to the SnO₂ PCA plot shown in Figure 6.8. It is clearly evident in the ZnO PCA plot that the concentration of carbon monoxide in the environment has a much greater effect on the metal-oxide resistance and corresponding gas sensor response for the ZnO nanoparticles compared to the SnO₂ nanoparticles. Therefore, there is not as tightly of a grouping or clustering of the data set to specific methane concentrations. This has some advantages and disadvantages for chemiresistive gas sensor technology. The drawback is that ZnO is not as selective to high methane concentrations in the presence of carbon monoxide as the SnO₂ nanoparticles. Zinc oxide displays more cross-sensitivity to the small concentrations of CO. In the development of an array, this can be used as an advantage because this sensor or element can be used to determine the CO concentration if the CH₄ concentration is known. The selection of the operating temperature for this element is difficult due to the non-uniformity in the PCA results. For the ZnO nanoparticles, 550°C was selected as the operating temperature to use for the sensor element in the array because it displayed the highest response which is beneficial for overcoming any signal to noise ratios in the sensor devices.

6.2.3 Selection of Array Elements

From the PCA study, the clustering of data was helpful to determine the operating temperature for each metal-oxide with the most differentiation between the methane and carbon monoxide gas concentrations. A four element sensor array was developed and is shown in Table 6.4. The operating temperature of each metal-oxide film is indicated in
the table as well as the detected gas that the material will be primarily used to detect in the proposed device.

<table>
<thead>
<tr>
<th>Material</th>
<th>Operating Temperature</th>
<th>Detected Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>500°C</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>600°C</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>NiO</td>
<td>450°C</td>
<td>CO</td>
</tr>
<tr>
<td>ZnO</td>
<td>550°C</td>
<td>CO</td>
</tr>
</tbody>
</table>

Table 6.4: Four element array based on metal-oxide nanoparticles used for detecting methane and carbon monoxide for coal mining applications.

The most important element of the sensor array is the SnO$_2$ nanoparticle sensor. At this operating temperature, methane gas is detected primarily with very little interference from the carbon monoxide gas concentrations. The TiO$_2$ element is similar in this behavior, but not as dominant as the SnO$_2$ sensor. By knowing the methane concentration which can be provided from the SnO$_2$ element, the NiO and ZnO elements can be used to define the carbon monoxide concentration in the system. The NiO and ZnO elements are cross-sensitive to both CH$_4$ and CO, but there is enough difference in the metal-oxide film resistance at the low carbon monoxide concentrations to effectively detect the analyte gas. The accuracy of each element in the sensor array to detect methane and carbon monoxide simultaneously will be presented in the next section.
6.3 Development of Prediction Model and Validation Testing

The gas sensor testing to this point in the dissertation has been performed to specified concentrations of analyte gases to determine the change in resistance of the metal-oxide film as a function of material, operating temperature, and analyte gas concentration. However, the desired operation of the gas sensor array occurs by measuring the resistance of the film and predicting the carbon monoxide and methane gas concentrations. A predictive model using linear relationships was developed and validation testing was performed to determine the accuracy of the model.

6.3.1 Linear Model for Detecting Methane and Carbon Monoxide

By using the gas sensor testing results for each metal-oxide material and the selected operating temperature after PCA, data existed for the creation of a linear-based prediction model. There are numerous predictive modeling techniques which involve sophisticated statistical analysis and require different amounts of calibration data in order to define the accuracy of the model. The goal of this work was to show the proof-of-concept that a linear prediction model could be constructed and tested to a new series of methane and carbon monoxide concentrations which had not been previously introduced.

In the DOE, the three concentrations of CO tested were 0, 35, and 100 ppm while the three concentrations of CH₄ tested were 0, 0.5, and 1%. The first linear model developed was for SnO₂ nanoparticles operated at 500°C which showed good sensor response to methane, but very little response to carbon monoxide. For the detection parameters of interest for coal mining applications the SnO₂ sensor element was treated as a selective sensor to methane concentrations. The average resistances of the SnO₂ film at the
methane concentrations in the DOE were as follows: baseline resistance was 23.30 MΩ, at 0.5% CH₄ the resistance was 2.73 MΩ, and at 1% CH₄ the resistance was 1.94 MΩ. There is a large disparity from the baseline resistance to the resistance of the oxide film at 0.5% methane. For this reason, there were two linear models developed for different regions of methane detection. The slope of the line was calculated for each region and this was given by the following set of equations.

\[
\frac{23.30 \text{M}\Omega - 2.73 \text{M}\Omega}{0\% \text{CH}_4 - 0.5\% \text{CH}_4} = -41.14 \frac{\text{M}\Omega}{\% \text{CH}_4} \quad (6.4)
\]

\[
\frac{2.73 \text{M}\Omega - 1.94 \text{M}\Omega}{0.5\% \text{CH}_4 - 1\% \text{CH}_4} = -1.58 \frac{\text{M}\Omega}{\% \text{CH}_4} \quad (6.5)
\]

The slopes of the lines for these two regions are significantly different. For the region of 0-0.5% CH₄, the following equation was used to predict the methane concentration for the SnO₂ sensor element operated at 500°C:

\[
\text{Resis tan ce}(\text{M}\Omega) = -41.14 \frac{\text{M}\Omega}{\% \text{CH}_4} \ast (\% \text{CH}_4) + 23.30 \text{M}\Omega \quad (6.6)
\]

Rearranging equation 6.6 yields the predictive model for SnO₂ for 0-0.5% CH₄, and this is given in equation 6.7:

\[
(\%) \text{CH}_4 = \frac{\text{Resis tan ce}(\text{M}\Omega) - 23.30 \text{M}\Omega}{-41.14 \frac{\text{M}\Omega}{\% \text{CH}_4}} \quad (6.7)
\]

The sign of the slope of the line is negative because the resistance decreases for an n-type semiconductor (SnO₂) in the presence of a reducing gas (CH₄). The predictive model for the SnO₂ sensor at the higher concentrations of CH₄ was calculated in a similar manner.
While the SnO$_2$ sensor was selective to methane, the creation of a predictive model for the ZnO and NiO sensor elements is more complex due to the cross sensitivity to both reducing gases. The calculation for the NiO prediction model will be presented with the ZnO model constructed in a similar manner. The resistance of the NiO film tested to the DOE was much more linear than the SnO$_2$ film to both CH$_4$ and CO concentrations. As a result, the equations were developed over the entire range for both gases. The calculation of the predictive model for NiO is provided in the following set of equations:

\[
\frac{3.65M\Omega - 3.83M\Omega}{0\%CH_4 - 1\%CH_4} = 0.18 \frac{M\Omega}{\%CH_4}
\]  

\[
\frac{3.65M\Omega - 3.86M\Omega}{0 \text{ ppmCO} - 100 \text{ ppmCO}} = 0.0021 \frac{M\Omega}{\text{ppmCO}}
\]  

(6.8)  

(6.9)

Since both analyte gases affect the resistance of the NiO film, the linear relationship will depend on both variables. However, the methane concentration can be determined using the SnO$_2$ sensor element and this can be used in the model for the NiO sensor element to predict carbon monoxide. The resistance of the NiO sample determined by the DOE for simultaneous methane and carbon monoxide concentrations is given by equation 6.10.

\[
\text{Resistance}(M\Omega) = 0.18 \frac{M\Omega}{\%CH_4} \times (\%CH_4) + 0.0021 \frac{M\Omega}{\text{ppmCO}} \times (\text{ppmCO}) + 3.65M\Omega
\]  

(6.10)

Rearranging equation 6.10 yields the predictive model for determining CO concentrations for the NiO sensor element operated at 450°C.
\[
(\text{ppmCO}) = \frac{\text{Resistive (MΩ)} - 0.18 \frac{MΩ}{%CH_4} \times (%CH_4) - 3.65MΩ}{0.0021 - \frac{MΩ}{ppmCO_4}}
\]  

(6.11)

6.3.2 Validation Testing

The models generated through the first DOE for each material needed to be tested to validate the accuracy of the predictive model. A new design of experiments was constructed to test the model to new concentrations of carbon monoxide and methane which had not been previously tested. The material and operating temperature were held constant during the validation testing and the two independent variables (CO concentration and CH\textsubscript{4} concentration) were identified through the dependent variable (metal-oxide film resistance). The design matrix for the validation tests is shown in Table 6.5. There were five levels for each gas for a total of 25 states tested. Three replicates were also completed for the design matrix and the average of the results for the three tests was used in the analysis of the predictive model.
Table 6.5: Design of experiments and levels for validation testing of linear model for each oxide.

<table>
<thead>
<tr>
<th>Level</th>
<th>CO Concentration</th>
<th>CH\textsubscript{4} Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 ppm</td>
<td>0 %</td>
</tr>
<tr>
<td>1</td>
<td>25 ppm</td>
<td>0.2%</td>
</tr>
<tr>
<td>2</td>
<td>75 ppm</td>
<td>0.4%</td>
</tr>
<tr>
<td>3</td>
<td>125 ppm</td>
<td>0.6%</td>
</tr>
<tr>
<td>4</td>
<td>200 ppm</td>
<td>0.8%</td>
</tr>
</tbody>
</table>

The DOE experiments for the validation testing were conducted using the microhotplate gas sensor test facility with the same conditions prescribed in the first DOE (namely time of each state). Predicted vs. actual concentrations of the analyte gases were investigated using the linear models developed in the previous section. Results of the SnO\textsubscript{2} nanoparticle sensor element operated at 500°C to the validation tests are shown in Figure 6.10. This sensor element is used to detect methane in the presence of carbon monoxide. This graph is plotted as methane concentration in percentage vs. randomized order that the validation test was operated at. The black squares depict the actual methane concentration governed by the validation test and given in Table 6.5. The red diamonds indicate the predicted methane concentration based off the resistance of the metal-oxide film and using the predictive model equation in equation 6.7.
Figure 6.10: Validation test for predictive model of SnO$_2$ nanoparticle sensor operated at 500°C for detection of CH$_4$.

The data from Figure 6.10 is rearranged in Figure 6.11 to give a better analysis of the validation testing. The x-axis was changed from the randomized run order to the state number for each test. A portion of the table describing the states during validation testing is given in Table 6.6. For the validation test of the SnO$_2$ sample, every five states the CH$_4$ concentration is increased by 0.2% while the CO concentration is increased at each methane level.
Figure 6.11: Validation test for predictive model of SnO$_2$ nanoparticle sensor operated at 500°C for detection of CH$_4$.

Table 6.6: Part of the table defining the state number and corresponding CH$_4$ and CO concentrations during validation testing.
The results of the validation test in Figure 6.11 are important for the development of gas sensor arrays for coal mining applications. This validation testing shows the predicted methane concentration of the SnO$_2$ sensor element is quite comparable to the actual CH$_4$ concentration. There is some variability between the gas sensor measurements, but all the predicted methane concentrations are within 0.1% of the actual concentration. In most cases the accuracy of the model is even better than that limit. This is better than the limit prescribed by MSHA which mandates that methane sensors in mines must be within 0.2% of the calibration gas.

Validation tests were conducted to the predictive model created for the NiO nanoparticle sample as well. This prediction model was developed for detecting carbon monoxide at low concentrations in the presence of elevated methane concentrations. The results of the validation test for the NiO sample operated at 450°C is shown in Figure 6.12. The predicted results for the first four CO levels of interest (0, 25, 75, and 125 ppm) are very comparable to the actual CO levels in the presence of CH$_4$. However, the predictive model is not suitable for the highest concentration of CO tested (200 ppm). There are a few possible explanations for the breakdown of the prediction model at this high concentration of CO. The most likely is that the prediction model was calibrated using a range of 0-100 ppm of carbon monoxide. Extrapolation of the prediction model to 200 ppm CO is not reliable based on the stated linear prediction model in equation 6.11.
Figure 6.12: Validation test for predictive model of NiO nanoparticle sensor operated at 450°C for detection of CO.

There are several studies that can be accomplished to improve the quality of the predictive model. The quality and quantity of available data can be improved by running more tests to the chemiresistive sensors at a larger range of analyte gas concentrations. As new control data are established, it may be desirable to merge these with the original calibration data and recalibrate in order to improve the predictive model.
6.4 Conclusions and Future Work

This final chapter of the dissertation explores the development of a 4-element metal-oxide nanoparticle based array for simultaneously detecting methane and carbon monoxide for coal mining applications. The studies performed in this section were a culmination of the results and technology investigated from the previous chapters, particularly Chapter 4 and 5. It is beneficial to describe the conclusions found in each chapter, because they contribute to the findings determined in this final chapter.

Chapter 1 presented the importance and motivation for the experiments carried out throughout the dissertation, namely that the author was interested in exploring gas sensor detection of methane and carbon monoxide in underground coal mines for explosion prevention and toxicity, respectively. The implementation of miniaturized gas sensor substrates in the form of microhotplate platforms was identified for an area of improvement in sensor technology for benefits of increased portability and reduced power consumption of the chemiresistive gas sensor device. Chapter 2 provided a background of existing chemiresistive gas sensor technology which specifically focused on the role of particle size, morphology, and microstructure of the metal-oxide film and how these affected the gas sensor performance for detection of analyte gases. Much of the published literature described the negative aspects of using metal-oxide nanoparticles because the material prefers to agglomerate, form secondary particles, and this reduces the gas sensing performance of the material.

The focus of this research was to understand how the particle size, morphology, and microstructure of the metal-oxide film affected the gas sensor performance to the two
gases of interest on miniaturized gas sensor devices in the form of microhotplate platforms. This was done through three main research studies. Chapter 3 involved the growth of SnO$_2$ nanowires from SnO$_2$ particles using an Au-catalyst. Growth conditions including temperature, time, and oxygen partial pressure were explored to determine the formation aspects of the SnO$_2$ nanowires. Gas sensor studies were completed that provided evidence that the SnO$_2$ nanowires increased detection to a fixed concentration of carbon monoxide compared to SnO$_2$ particles without nano-structure formation. Metal-oxide nanoparticles were synthesized and characterized in Chapter 4 in order to deposit nanoparticle films via ink-jet printing on microhotplate platforms in a reproducible manner. The ink-jet printing parameters relied heavily on the rheological properties of the nanoparticle-laden ink. The deposited film had a highly porous microstructure which was free of agglomeration and secondary particle formation.

A second research study was performed in Chapter 5 to compare the gas sensor performance of SnO$_2$ nanoparticles, hierarchical particles, and micron-size particles. The nanoparticles were developed into an ink and deposited via ink-jet printing on the microhotplate substrates provided by the details in Chapter 4 to control the microstructure of the metal-oxide film. By preventing agglomeration of the nanoparticle film, the SnO$_2$ nanoparticles displayed similar gas sensor performance to methane and carbon monoxide as the hierarchical particles. Both nano-structures had much higher gas sensor response than the micron-size particles which confirms the surface area of the metal-oxide film is critical for reaction of the analyte gas at the surface.
The last research study presented in this chapter of the dissertation describes the development of a nanoparticle array for detecting methane and carbon monoxide in the presence of one another. A DOE was constructed and PCA was used for determining the optimum temperatures of the metal-oxide elements. Design of experiments is a method used for testing a series of variables in order to understand the interaction of variables. The four variables tested in the DOE were metal-oxide material, operating temperature, CH₄ concentration, and CO concentration. Principal component analysis was used to analyze the multi-dimensional data in order to determine the operating temperature for each metal-oxide film for the most variability between the CO and CH₄ gas concentrations.

A 4-element array was developed with SnO₂ and TiO₂ able to selectively detect the high methane concentrations of interest. ZnO and NiO were used as elements in the array because the gas sensor was cross-sensitive to both gas types. By using the SnO₂ and TiO₂ elements which provided information on the methane concentrations, the ZnO and NiO sensor elements were able to provide data on the carbon monoxide concentrations. A linear based prediction model was developed for each material and tested for accuracy and reproducibility of the model to a series of random gas concentrations. The validation test results showed fairly good accuracy of the prediction model, and breakdown of the model only occurred when the model was attempted to extrapolate to high levels of carbon monoxide.
There are several more studies that could be completed for the development of gas sensor array devices for detecting carbon monoxide and methane for coal mining applications. Most of these involve creating a prediction model which is more accurate to a larger range of methane and carbon monoxide concentrations. While Chapter 6 provided a proof-of-concept for using the metal-oxide nanoparticles deposited on microhotplate substrates via ink-jet printing for predictive modeling of CO and CH₄, the advancement of the technology for commercial applications would require a more complete set of calibration data.

The creation of a 2x2 sensor array based on miniaturized sensor platforms similar to the Kebaili microhotplates would be needed to contain all four sensor elements on one device. The device could be similar to the current technology NIST has for their 4x4 microhotplate arrays. This is important to note because sensor geometries, particularly the distance between the electrodes, will affect the resistance of the metal-oxide film. Resistance is not an inherent material property and the value depends on the cross-sectional area and length between the electrodes. The model for predicting the carbon monoxide and methane concentrations uses the resistance of the metal-oxide elements. Therefore, the oxide particle size, morphology, microstructure of the oxide film, operating temperature, and sensor geometry will affect the prediction model. Additional testing would be needed to produce a predictive model for a more commercially viable device which contains all four sensor elements.

In addition to an established sensor array device with all four sensor elements, the construction of a better model could be performed using non-linear statistical analysis.
The high concentrations of methane for the coal mining application make it difficult to use completely linear aspects in the development of a prediction model. At high analyte concentrations, saturation of the gas can occur and the relationship between resistance and gas concentration may not be linear. Other multivariate calibration techniques could be used as pretreatment to make the data more linear, or a non-linear predictive model could be created.

An extensive study also needs to be completed in order to confirm the inter-device reproducibility between samples of the same type (material, operating temperature). A brief description of the reproducibility for SnO₂ nanoparticle films deposited on microhotplate platforms via ink-jet printing was provided in Chapter 4. The baseline resistance of the metal-oxide film was tested between three samples as a function of temperature with good reproducibility between the samples. However, for the development of a commercial device, a vast experimental study and most likely DOE would need to be tested for inter-device reproducibility. The variables that must be kept constant to ensure reproducibility for the nanoparticle based array are particle size, morphology, amount of material deposited on the sensor platform, geometry of the sensor substrate, and operating temperature. The microstructure of the nanoparticle based oxide film has been shown to be reproducible using the ink-jet printing deposition system.
References


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Appendix A: Characterization Details

*X-ray Diffraction*

Powder x-ray diffraction (XRD) patterns were obtained using a Scintag XDS 2000 diffractometer. Copper x-rays (Cu Kα) of wavelength 1.5406 Å were used in all experiments. XRD patterns were collected at room temperature using a continuous scan over an angular range of 2θ =10°-90° with step size of 0.03° and scan rate of 1 /minute. The broadening was determined using Jade Software (Materials Data, Inc., Livermore, CA) version 5.0 by measuring the peak breadth at full-width half-maximum (FWHM) and using the simulation function available in the software to simulate a diffraction pattern from a known crystallite size.

*Scanning Electron Microscopy*

Scanning electron microscopy was done in a FEI Sirion field emission gun scanning electron microscope. The samples were coated with a thin layer of gold deposited via sputtering prior to analysis. This was done to reduce the charging effect of the metal-oxides when bombarded by electrons. The accelerating voltage was generally maintained at 5 kV with a spot size of 3.

*Thermal Gravimetric Analysis*
Thermal gravimetric analysis measurements were collected using a Perkin Elmer TGA 7 equipped with a platinum crucible. Samples were heated from room temperature (~24°C) 237 to 1000°C with a heating rate of 5°C/minute while the chamber was continuously purged with air at a rate of 25 sccm.

Brunauer Emmett-Teller (BET) Surface Area

A Micromeritics ASAP 2020 instrument was used for the BET surface area measurements. Samples were degassed under vacuum at 200°C for a period of at least twelve hours and no longer than twenty four hours prior to surface area measurements. The multi-point BET surface area was estimated from the adsorption isotherm for relative (partial) pressures <0.35 using integrated software contained within the Micromeritics system.
Appendix B: Microhotplate Platform from Kebaili

The dimensions for the KMHP-100 microhotplates are listed below. The micromachined silicon die is packaged in a gold plated TO-18 package via gold ball wire bonding.

KMHP-100 die – 1000 μm x 1000 μm

Silicon nitride layer membrane – 500 μm x 500 μm

Platinum micro-heater - 250 μm x 250 μm

Figure B.1: KMHP Microhotplate from the Kebaili corporation.
The thin film resistive platinum micro-heater uses the Joule effect to convert electrical power to heating power. The micro-heater can be biased by a direct current (DC) voltage source.

Figure B.2: Temperature versus micro-heater voltage (mV) for the Kebaili microhotplate platform.

An equation was used in the LabVIEW program during testing to convert the desired operating temperature in degrees Celsius to a voltage. This was calculated using the temperature vs. voltage curve above in Figure B.2 to be \( V=0.067\times T+0.234\). For the resistance calculation of the metal-oxide film, 1.00 mA was set across the electrodes and through the metal-oxide film for the resistance measurement.
Appendix C: Calculation of Oxygen during Gas Sensor Testing

The series of equations below describes the calculations to control the oxygen content during gas sensor testing in the microhotplate gas sensor test facility. The oxygen content is extremely important in gas sensor testing because it affects the quantity of adsorbed oxygen species on the surface of the metal-oxide film which, in turn, is critical for the resistance measurement of the oxide. Oxygen content is 20.8% by volume in air. For this discussion, the symbols for each gas correspond to the flow rate of each gas in the microhotplate gas sensor facility introduced through digital mass flow controllers (MFCs). For example, $O_2$ is the flow rate of the oxygen mass flow controller, MFC.

\[ .208Air_{mix} = O_2 \]
\[ .792Air_{mix} = N_{2}^{tot} \]
\[ Air_{mix} = \frac{O_2}{.208} \]
\[ Air_{mix} = \frac{N_2^{tot}}{.792} \]
\[ \frac{N_2}{.792} = \frac{O_2}{.208} \]
\[ O_2 = .2626N_2^{tot} \]

\[ O_2 + N_2 = 1000 - CH_4 - CO \]
\[ N_2 = 1000 - CH_4 - CO - O_2 \]
The following equation is used for oxygen concentration (flow rate) in gas sensor testing. This is used because the methane cylinder used in testing is 10% by volume and the carbon monoxide cylinder is 500 ppm by volume. Both cylinders are balanced with inert gases.

\[
O_2 = 0.2626(N_2 + 9CH_4 + 0.995CO)
\]

\[
N_2 = 1000 - CH_4 - CO - [0.2626(N_2 + 9CH_4 + 0.995CO)]
\]

\[
N_2 = 1000 - 1.2636CH_4 - 1.23636CO - 0.2626N_2
\]

\[
1.2626N_2 = 1000 - 1.2636CH_4 - 1.23636CO
\]

The following equation is used for nitrogen concentration (flow rate) in gas sensor testing. Based on CH\textsubscript{4} and CO flow rates, the “make up” nitrogen is added. Subsequently the oxygen content (flow rate) is calculated based on the N\textsubscript{2} makeup, CH\textsubscript{4}, and CO flow rates.

\[
N_2 = \frac{(1000 - 1.2636CH_4 - 1.23636CO)}{1.2626}
\]