Interaction of Metal Oxides with Carbon Monoxide and Nitric Oxide for Gas Sensing Applications

DISSERTATION

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By

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Abstract

This dissertation involves the study of the interaction of carbon monoxide (CO) and nitric oxide (NO) on derivatives of low temperature conducting metal oxides, ruthenium and vanadium oxides. The interactions of these gases with the metal oxides lead to changes in conductivity which show promise for possible applications as a new class of resistive based ambient gas sensors that alleviate the current limitations of CO and NO sensors that operate at elevated temperatures. These sensors are based on hydrated ruthenium oxide (RuO$_x$(OH)$_y$) and vanadium pentoxide (V$_2$O$_5$).

RuO$_x$(OH)$_y$ was prepared a wet precipitation reaction involving ruthenium chloride with a base. This material was amorphous, made up of 20–50nm particles and contains Ru(III) and Ru(IV), as determined by XPS. Thick films were made of air and supercritical dried particles of RuO$_x$(OH)$_y$. The conductivity of these films decreased in the presence of CO in air and this change was reversible. Infrared spectroscopy showed the formation of carbonates and water in the presence of CO, which disappeared upon replacement of CO with air. Upon thermal treatment of RuO$_x$(OH)$_y$ above 200°C, a decrease in the conductivity change in the presence of CO at room temperature is observed. These changes were accompanied by a conversion of the amorphous RuO$_x$(OH)$_y$ to a crystalline RuO$_2$ and consequently a conversion of Ru(III) to Ru(IV). This dissertation proposes the oxidation of CO on RuO$_x$(OH)$_y$ leads to reduction of the ruthenium and subsequently a decrease in conductivity of the thick films. With the conversion to crystalline RuO$_2$, the
material becomes metallic and conductivity changes are diminished. Changes in RuO$_x$(OH)$_y$ conductivity with CO provides an opportune platform for an ambient CO sensor. The interferences from ambient concentrations of hydrocarbons, ammonia, CO$_2$, NO and NO$_2$, were shown to have no effect on the conductivity.

This dissertation also discusses the study of the interaction of NO with vanadium oxides. The V$_2$O$_5$ was used as received and the vanadium dioxide (VO$_2$) was synthesized by reduction of V$_2$O$_5$. The materials were both crystalline particles of 5 µm in V$_2$O$_5$ and 1x5 µm rods in VO$_2$. The composition was determined to be predominantly V(V) in V$_2$O$_5$ and V(V) and V(IV) in VO$_2$, as determined by XPS. Thick films of V$_2$O$_5$ were made and the conductivity of these films decreased in the presence of 15 ppm NO and increased in the presence of 500 ppm NO in air reversibly. While the conductivity of VO$_2$ decreased in the presence of 15 and 500 ppm NO. Upon heating V$_2$O$_5$ to > 350°C, an increase in the conductivity is observed irrespective of concentration. This dissertation proposes the chemisorption of NO on the surface of V$_2$O$_5$ which leads to a change in the bulk donor density on the surface manifested as an inversion layer. This n→p transition explains the change in conductivity observed on V$_2$O$_5$ with NO which does not occur on VO$_2$ due to its metallic conductivity. The interferences from ambient concentrations of propane, ammonia, CO and acetone were shown to have no effect on the conductivity.
Dedication

This document is dedicated to my wonderful supportive husband, Kehinde Oluwatobiloba Adeyemo-Ayodele. Thank you for all your unconditional love and support. This is just the beginning and the sky is the limit.

My loving and encouraging parents, Mr Adedokun Adeyemo and Mrs Yetunde Adeyemo who always told me I could achieve my dreams and goals with hard work and prayers. Thank you for all the sacrifices you made to make my dreams come true.

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**Fields of Study**

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Table of Contents

Interaction of Metal Oxides with Carbon Monoxide and Nitric Oxide for Gas Sensing Applications ........................................................................................................... 1

DISSERTATION ........................................................................................................... 1

Abstract .................................................................................................................. ii

Dedication ............................................................................................................... iv

Acknowledgments .................................................................................................... v

Vita ............................................................................................................................ vii

Publications ............................................................................................................. vii

Fields of Study ........................................................................................................ viii

Table of Contents ................................................................................................... ix

List of Tables .......................................................................................................... xiv

List of Figures ......................................................................................................... xv

CHAPTER 1: INTRODUCTION ...................................................................................... 1

1.1. Importance and Applications of Gas Sensors ..................................................... 1

1.2. Types of Gas Sensors ....................................................................................... 2

1.2.1. Sensing Strategies ....................................................................................... 2
1.3. Resistive Gas Sensors

1.3.1. Metal Oxide Semiconductor based Resistive Gas Sensors

1.4. Optimizing Metal Oxide Gas Sensors

1.4.1. Sensing Platform Orientation

1.4.2. Lowering Temperature for Gas Sensing by Materials fabrication

1.4.3. Lowering Temperature for Gas Sensing by Control of Particle Size

1.4.4. Lowering Temperature for Gas Sensing by Additives in Metal Oxide Semiconductor Sensors

1.4.5. Lowering Temperature for Gas Sensing by Control of Crystal Defects

1.5. Sensing Combustible Gases

1.5.1. Need for Carbon Monoxide Sensors

1.5.2. Need for NOx Sensors

1.6. Low Temperature Gas Sensors

References

CHAPTER 2: HYDROUS RUTHENIUM OXIDE AS A PLATFORM FOR CARBON MONOXIDE SENSING AT AMBIENT CONDITIONS

2.1. Introduction

2.2. Experimental

2.2.1. Materials Synthesis
2.2.2. Materials Characterization ................................................................. 39
2.2.3. Resistance Measurements ................................................................. 40

2.3. Results ........................................................................................................ 41
2.3.1. Synthesis and Characterization of RuO_x(OH)_y ................................. 41
2.3.2. Interaction of RuO_x(OH)_y with CO ................................................... 43
2.3.3. Change in Properties of RuO_x(OH)_y with Heat Treatment .......... 45
2.3.4. CO Sensing Potential of RuO_x(OH)_y under Ambient Conditions .... 46
2.3.5. Device Optimization ................................................................. 47
2.4.1. Reactivity of CO with RuO_x(OH)_y .................................................... 50
2.4.2. Sensor Performance ................................................................. 54
2.4.3. Performance of Supercritical Dried Ru_x(OH)_y .............................. 55

2.5. Conclusion ............................................................................................. 56

References ........................................................................................................ 57

CHAPTER 3: DEVELOPMENT OF A VANADIUM OXIDE BASED ROOM

TEMPERATURE ROOM TEMPERATURE NO SENSOR ........................................ 82

3.1. Introduction ................................................................................................ 82

3.2. Current Sensors for NOx Detection ....................................................... 84
3.2.1. Lessons Learned from Hydrated Ruthenium Oxide (RuO_x(OH)_y) .... 84

3.3. Properties of Vanadium Oxides .............................................................. 85
3.3.1. Interaction of NO with Vanadium pentoxide ........................................... 86

3.4. Gas Sensing Applications of Vanadium Oxides .......................................... 86

3.4.1. Sulfur Dioxide (SO\textsubscript{2}) ................................................................. 87
3.4.2. Hydrocarbons ........................................................................................... 87
3.4.3. Humidity and Ethanol .............................................................................. 87
3.4.4. Carbon Monoxide ................................................................................... 89
3.4.5. Amines and Ammonia ........................................................................... 89
3.4.6. Nitric Oxide and Nitrogen Dioxide ......................................................... 90

3.5. Experimental Section .................................................................................. 92

3.5.1. Materials Synthesis .................................................................................. 92
3.5.2. Materials Characterization ....................................................................... 92

3.6. Results ......................................................................................................... 94

3.6.1. Materials .................................................................................................. 94
3.6.2. Characterization of V\textsubscript{2}O\textsubscript{5} ..................................................... 94
3.6.3. Characterization of VO\textsubscript{2} ............................................................... 95
3.6.4. Resistance Change with NO ................................................................. 95
3.6.5. Viability as a Gas Sensor ........................................................................ 100

3.7. Discussion .................................................................................................... 100

3.7.1. NO Interaction with Vanadium Oxide ............................................... 100
3.7.2. Viability of V$_2$O$_5$ as An Ambient Gas Sensor for NO.............................. 106

3.8. Conclusion........................................................................................................... 107

It is interesting to contrast the CO sensor using RuO$_x$(OH)$_y$ and NO sensor using V$_2$O$_5$. In the former case, it is a chemical reaction catalyzed by the Ru that results in the sensing response, whereas for the latter, it is chemisorption that is controlling the response. However, in both cases, the presence of lower oxidation states of the metal are relevant. For the CO, it facilitates the oxidation, whereas with NO, it promotes the conductivity and the electrons involved in the chemisorption................................. 107

References .................................................................................................................. 108

CHAPTER 4 FUTURE DIRECTIONS: SENSOR PERFORMANCE/MECHANISM 131

4.1.1. Optimization of Porosity................................................................................. 131

4.1.2. Catalytic Reactions .......................................................................................... 132

4.1.3. Mechanistic Studies :Role of water ............................................................... 132

4.2. Vanadium Pentoxide ......................................................................................... 133

4.2.1. Increase Porosity ............................................................................................ 133

4.2.2. Molecular Mechanism Determination .......................................................... 133

4.2.3. Sensor Performance ....................................................................................... 134

References.................................................................................................................. 135

Bibliography .............................................................................................................. 136
List of Tables

Table 1.1 Summary of low temperature carbon monoxide gas sensors ...................... 25
Table 1.2 Summary of low temperature NO and NO$_2$ sensors ................................ 27
Table 2.1 Vibrational frequencies of carbonyl, carbonate and bicarbonate species ....... 62
Table 2.2 Critical temperature ($T_c$) and pressure ($P_c$) of fluids ............................ 63
Table 3.1 Conductive metal oxide candidates for low temperature gas sensing and their properties ..................................................................................................................... 112
List of Figures

Figure 1.1 Different sensor platforms for metal oxide semiconductor sensors from reference [76]. .......................................................................................................................................................... 29

Figure 1.2. Two metal oxide semiconductor particles showing the formation of the surface depletion layer upon exposure to oxygen................................................................. 30

Figure 1.3. Interaction of two MOS particles forming depletion layers when exposed to (a) oxidizing gas oxygen (b) reducing gas carbon monoxide. ........................................ 31

Figure 1.4. Different electrode constructs with metal oxide semiconductor (MOS) deposited. Design is similar in resistive, capacitive and IV coupled devices.................. 32

Figure 1.5. Field effect-transistor devices for gas sensing based on reference [15]. .... 33

Figure 1.6. Schematic of a surface acoustic wave device for gas sensing applications. .. 34

Figure 1.7 Amperometric CO sensor from reference [50]. (a) Top view (b) Sensor cross section (C.E., counter electrode, W.E., working electrode and R.E., reference electrode). ....................................................................................................................................... 35

Figure 1.8. Potentiometric Sensor.................................................................................. 36

Figure 2.1.(a) Drop coating of a suspension of RuO$_x$(OH)$_y$ on to an interdigitated gold electrode in the fabrication of a carbon monoxide gas sensor, (b) electrode before and after coating (c) interdigitated gold electrode dimensions............................................................ 64

Figure 2.2. Schematic of experimental gas sensor testing apparatus......................... 65
Figure 2.3. (a) Thermogravimetric analysis of RuO$_x$(OH)$_y$ (ramp rate of 10°C/min in a nitrogen gas flow of 75 cc/min) (b) XRD pattern of RuO$_x$(OH)$_y$, (c) TEM image of RuO$_x$(OH)$_y$. ................................................................. 66

Figure 2.4 XPS spectra of RuO$_x$(OH)$_y$, (a) O 1s region : Δ Ru-O-Ru, ▲ Ru-OH and Ru-H$_2$O, Ru-carbonate (b) Ru 3d region Δ Ru(III) ▲ Ru(IV) and □ carbon 1s carbonaceous impurities and carbonates................................................................. 67

Figure 2.5 Changes in resistance of RuO$_x$(OH)$_y$ with repeated exposure of to 250 ppm CO in 21% Oxygen at 25°C.................................................................................................................................................. 68

Figure 2.6. Diffuse reflectance infrared spectra of RuO$_x$(OH)$_y$, (a) initial spectra, (b) spectra after first exposure to O$_2$ (21%) for 150 min, (c), spectra after CO (2000 ppm in air) exposure for 15 min, (d) spectra closed off for 45 min after O$_2$ for 30 min (e) Second exposure to O$_2$ (21%) for 150 min (f) Exposure of (b) to CO$_2$ (25°C) ........................................... 69

Figure 2.7 Diffuse reflectance infrared difference spectra of RuO$_x$(OH)$_y$ between (a) two O$_2$ (21%) exposures (prior and after CO exposure) (b) O$_2$ (21%) and CO (2000 ppm in air) exposure (c) O$_2$ (21%) and 45 min after 30 min O$_2$ exposure to (b) (d) O$_2$ and CO$_2$ exposure .................................................................................................................................................. 70

Figure 2.8. XRD pattern of samples obtained by heating RuO$_x$(OH)$_y$ to different temperatures (data recorded at 25°C)......................................................................................................................... 71

Figure 2.9. (a) Ru 3d XPS spectrum of RuO$_x$(OH)$_y$ heated at 25-600°C, (b) O 1s XPS spectra of RuO$_x$(OH)$_y$ heated at 25-600°C (c) Ru 3d XPS spectra of RuO$_x$(OH)$_y$ heated to 600°C : Δ Ru screened final state ▲ Ru unscreened final state for Ru(IV). (d) O 1s XPS spectra of RuO$_x$(OH)$_y$ heated to 600°C : Δ Ru-O-Ru, ▲ Ru-OH and Ru-H$_2$O 72
Figure 2.10. (a) Change in resistance of samples obtained by heating RuO$_x$(OH)$_y$ (25-600°C) upon exposure to 500, 250 and 1000ppm CO at 25°C (b) Normalized resistance change of samples obtained by heating RuO$_x$(OH)$_y$ (25-600°C) upon exposure to 250, 500 and 1000 ppm CO at 25°C (R is resistance in CO and R$_o$ is resistance in background gas 21% Oxygen) ........................................................... 73

Figure 2.11. Change in resistance of three different samples of RuO$_x$(OH)$_y$ upon exposure to 1000, 500, 250 and 1000 ppm CO at 25°C in 21% oxygen. Inset: Normalized change in resistance on exposure to 32 ppm CO at 25°C in 21% oxygen. ........................................... 74

Figure 2.12. Normalized change in resistance of RuO$_x$(OH)$_y$ on exposure to 250ppm CO, 2000ppm CO$_2$, 1000ppm Methane and Propane, 150ppm Ammonia, 15ppm NO and 15ppm NO$_2$ at 25°C ............................................................................................................. 75

Figure 2.13. Pressure – Temperature phase diagram for carbon dioxide (CO$_2$) .......... 76

Figure 2.14. (a) Gold interdigitated electrodes before deposition of RuO$_x$(OH)$_y$ , (b) Electrodes after deposition of equal amounts of RuO$_x$(OH)$_y$ and (c) Electrode super critically dried on the left and electrode air dried on the right............................................ 77

Figure 2.15. The effect of exchange solvent on super critically dried RuO$_x$(OH)$_y$ .......... 78

Figure 2.16. The effect of film thickness on response and recovery times on super critically dried RuO$_x$(OH)$_y$ ......................................................................................... 79

Figure 2.17. Percolative fashion of electron transport in hydrated ruthenium oxide from reference [13] .................................................................................................................. 80

Figure 3.1 SEM of vanadium pentoxide (V$_2$O$_5$) ......................................................... 113

Figure 3.2. Diffraction pattern of vanadium pentoxide (V$_2$O$_5$) ................................. 114
Figure 3.3. XPS of vanadium pentoxide (V₂O₅) ................................................................. 115
Figure 3.4 SEM of vanadium dioxide (VO₂) ................................................................. 116
Figure 3.5 XRD of vanadium dioxide (VO₂) ................................................................. 117
Figure 3.6. XPS of vanadium dioxide (VO₂) ................................................................. 118
Figure 3.7. Room temperature test of vanadium pentoxide (V₂O₅) with 15 ppm NO then
500 ppm NO in 21% oxygen ............................................................................................. 119
Figure 3.8. Room temperature test of vanadium pentoxide (V₂O₅) with 500 ppm NO then
15 ppm NO in 21% oxygen ............................................................................................. 120
Figure 3.9. Effect of heat treatment on resistance change to 15 ppm NO on vanadium
pentoxide (V₂O₅) ............................................................................................................. 121
Figure 3.10. Effect of heat treatment on resistance change to 500 ppm NO on vanadium
pentoxide (V₂O₅) ............................................................................................................. 122
Figure 3.11. Summary of vanadium pentoxide (V₂O₅) heat treatment and resistance
changes with the interaction of 15 ppm and 500 ppm NO. ............................................. 123
Figure 3.12. Effect of heat treatment on resistance changes to 15 ppm NO on vanadium
dioxide (VO₂) in 21% oxygen .......................................................................................... 124
Figure 3.13. Effect of heat treatment on resistance changes to 500 ppm NO on vanadium
dioxide (VO₂) in 21% oxygen ........................................................................................ 125
Figure 3.14. Vanadium pentoxide (V₂O₅) at 400°C exposed to 15 ppm and 500 ppm NO
in 21% oxygen ................................................................................................................ 126
Figure 3.15 Selectivity of Vanadium pentoxide, (V₂O₅) to carbon monoxide at 25°C and
400°C.................................................................................................................................. 127
Figure 3.16. Selectivity study on vanadium pentoxide (V₂O₅) at 25°C in 21% oxygen. 128

Figure 3.17. Diffuse reflectance infrared difference spectra of vanadium pentoxide (V₂O₅)
(a) surface exposed to O₂ (21%) exposure (b) O₂ (21%) and NO (1000 ppm) and (c)
Difference between (a) and (b) .......................................................... 129

Figure 3.18. Scheme modified from reference [41] showing energy-level diagram of an n-type semiconductor (a) dry nitrogen atmosphere, which corresponds to a flatband situation (b) Oxygen adsorption leads to the surface states which are occupied by the electrons, this results either in a depletion layer and reduced n-type surface conductivity (c) or in an inversion layer (the Fermi level $E_F$ lies below the intrinsic level $E_i$) and p-type surface (Donor Levels not shown) ........................................ 130
CHAPTER 1: INTRODUCTION

1.1. Importance and Applications of Gas Sensors

As the world has become industrialized, the need for gas sensors has increased. Along with the demands for these devices, the standards for reliability, selectivity, cost, miniaturizability, safety, and minimal energy requirements have also intensified. Gas sensors have become invaluable to industrial process monitoring of highly complex combustion processes, such as internal combustion engines, boilers, automotive, paper, glass and ceramic manufacturing, and heat treatment processes. Also power plants such as coal, nuclear and renewable energy have processes that have come to rely on gas sensors to optimize power production and minimize losses. Other applications include environmental monitoring for early fire detection, air quality control in enclosed spaces, flammable gas monitoring and home appliance usage. The requirements for quick data processing and control in these applications also heighten the need for rapid real time gas sensors. Market research experts such as BCC Research LLC published a report stating that the global market for sensors was estimated at $56.3 billion in 2010. It is expected to increase to $62.8 billion in 2011 and then to nearly $91.5 billion by 2016, at a compound annual growth rate (CAGR) of 7.8%. They also estimated the market for biosensors and chemical sensors is expected to experience the highest growth, at a CAGR of 9.6% during the 5-year period from 2011 to 2016, projecting this sector to be worth $13 billion in 2011 and $21 billion in 2016 [1]. In the past 20 years, considerable research has been directed to the development of gas sensors for the detection of air pollutant gases, which include the oxides of nitrogen (NO\(_x\)), oxides of carbon (CO/CO\(_2\)), oxides of sulfur (SO\(_x\)), and other hydrocarbon gases
such as methane [2]. These gases are emitted into the atmosphere from industrial and domestic processes all over the world and hence the use of gas sensors in streamlining process and improving efficiency, so existing natural resources may be preserved as new developments are made in technology.

1.2. Types of Gas Sensors

1.2.1. Sensing Strategies

1.2.1.1. Gas chromatography/mass spectrometry

There are several ways in which a gas can be monitored, including methods, such as gas chromatography/mass spectrometry (GC/MS), which involves the initial separation of a mixture of gas analytes based on the interaction with a stationary phase followed by mass spectral analysis [3].

1.2.1.2. Chemiluminescence

Chemiluminescence analyzers can be used when the analyte gas reacts with ozone, as in the case of nitrogen oxides. The reaction product is formed as an excited molecule, which relaxes by emitting radiation in the wavelength between 600-2800 nm, and can be monitored by a photomultiplier tube [4]. This method is used in research applications, in large industrial gas detection and clinical settings.

1.2.1.3. Optical methods

Optical methods, such as infrared spectroscopy have also been used for the detection of gases. The changes in the vibrational and rotational frequencies upon absorption of infra red radiation is specific to the analyte molecules, e.g., absorption for CO occurs at 2143 cm$^{-1}$ and NO at
1891 cm$^{-1}$ [5]. These methods can be very accurate but have their limitations in the ability to be miniaturized, need regular calibration and exhibit long term drift [6].

1.2.1.4. **Surface acoustic wave devices**

Devices such as surface acoustic wave devices (SAW) and quartz crystal microbalances consist of piezoelectric devices with a reactive film that interacts with the analyte gases. This interaction changes the mass of the film by adsorption, swelling or causing a chemical change resulting in a change of the frequency, amplitude or phase of oscillation of the piezoelectric support [7]. Depending on the nature of the film, the interaction of gas molecules will differ. Materials such as polymers, polymer composites [8-10], graphene, carbon nanotubes, metal oxides and metal oxide composites have also been used as the active sensing element. These devices have been shown to detect low gas concentrations at room temperatures but nonspecific binding of molecules limit the film by their selectivity and reproducibility.

1.2.1.5. **Electrochemical gas sensors**

Devices that detect analyte gases based on changes in electrical signals such as impedance, current, resistance and voltage are also used for gas sensing, these are classified under electrochemical gas sensors [11,12]. Field effect transistor (FET) devices are also used for gas sensing applications [13-15]. The sensor consists of three main parts, a source which provides current, a drain which allows current out and the gate which modulates the amount of current permitted to flow between the source and the drain. The application of a bias between the gate and the drain induces an electric field that affects the conductivity. In order to achieve sensitivity at lower operating temperatures, catalysts on gate materials and various gate materials may be used. Some examples are seen in Table 1.1 for CO [13, 15-17] and Table 1.2 for NO [14,18] sensors.
Electrochemical gas sensors can be further grouped into potentiometric, amperometric and resistive gas sensors. These devices vary based on the analyte signal that is measured upon exposure to target gases. Potentiometric sensors measure changes in potential difference between electrodes, amperometric sensors measure current flow between electrodes [19] and resistive sensors measure changes in the conductivity of the materials upon exposure to analyte gases [2]. Examples include metal insulator semiconductor (MIS) diodes, p-n junctions, metal oxide semiconducting (MOS) capacitors, resistive and ferroelectric devices. MOS gas sensors can be readily miniaturized and mass produced. Amongst these devices, MOS devices made of ceramics can be further classified based on the mode in which these electrical signals are obtained. The analyte gases may interact with the ceramic and induce bulk conductivity changes, metal / oxide junction conductivity changes or surface conductivity changes [2].

1.3. Resistive Gas Sensors

Resistive gas sensors are typically made up of films of particles of a MOS or conducting polymer deposited onto an insulating substrate containing metal electrodes for electrical measurements. As seen in Figure 1.1, the substrate can be made in different ways with different orientations and spacing of the electrodes, interdigitated, 4 point measurement and heated tube. A commonly used substrate is made of a metal such as gold interdigitated fingers with a spacing of 0.25 mm on a non conductive alumina support of dimensions 10 x 10 mm. The layer of MOS is typically of 100-500 µm thickness deposited on the alumina. This layer may consist of an organic polymer/polymer composite [20,21], carbon nanotubes [22,23] and MOS [24-33]. When exposed to analyte gases, surface chemical reactions occur that alter the conductivity of the material. Polymers and carbon nanotubes work well at low temperatures but are susceptible to changes in
humidity and sometimes require oxygen free atmospheres to operate. These interference issues can be minimized in MOS based devices, but these operate at temperatures >200°C.

1.3.1. Metal Oxide Semiconductor based Resistive Gas Sensors

Metal oxide semiconductor based gas sensors are widely studied, and show changes in electrical conductivity upon changes in the environment around the device [34]. The change in conductivity will occur with a change in oxygen partial pressure. Electrical changes can also be due to surface adsorption of analyte molecules leading to changes in defect concentrations in the MOS, interaction of gases with the surface adsorbed oxygen, thereby changing the density of charge carriers. These interactions may lead to changes in bulk conductivity, junction or surface layer conductivity.

1.3.1.1. Bulk conductivity

This occurs when ceramic materials have defects with high mobility or is at a temperature high enough that it can maintain its stoichiometry in equilibrium with the surrounding environment. The overall conductivity of a MOS is dependent on the given temperature and the oxygen partial pressure in the environment. Thus defect structure of the MOS determines the overall bulk conductivity. A defect site such as an oxygen vacancy within the MOS can react with surrounding oxygen and two electrons to form adsorbed oxygen on the surface as seen in equation 1.

\[
\frac{1}{2} O_2 + 2e^- + V_o^- \rightarrow O_{ads} (1)
\]

Where \(V_o^-\) represents the oxygen vacancies then the overall conductivity can be described by the following equation.
Where \( \sigma_0 \) is a constant, \( E_a \) the activation energy for conduction and \( n \), a positive or negative value, depending on the point defects due to oxygen removal from the crystal lattice of the MOS. \( k \) is the Boltzmann constant, \( T \) is temperature in Kelvin, \( p(O_2) \) the partial pressure of oxygen. A MOS with small values of \( n \) and activation energy would give a larger sensitivity to changes in oxygen partial pressure and exhibit with a lower dependence on temperature. TiO\(_2\) is an n-type semiconductor which is used in oxygen sensing in combustion applications [35]. It can detect a wide range of oxygen sensing \( P(O_2) \) (1-1\(^{0}\) atm). The mechanism of sensing action arises due to the ability of the rutile crystal lattice to contain oxygen vacancies (\( V_o^+ \)) and interstitial Ti\(^{3+}\) and Ti\(^{4+}\). The formation of these interstitials produces conducting electrons as seen in the following reactions.

\[
TiO_2 \rightarrow Ti^{3+} + 3e^- + O_2 (3)
\]

\[
TiO_2 \rightarrow Ti^{4+} + 4e^- + O_2 (4)
\]

As evident from equations 1, 3 and 4, increasing the oxygen partial pressure would lead to a decrease in the bulk conductivity of TiO\(_2\), which is what is expected of an n-type MOS.

### 1.3.1.2. Surface conductivity

Surface conductivity changes are usually more sensitive to changes in oxygen partial pressure than bulk conductivity changes [2]. Change in the concentration of conduction electrons on the surface of a MOS occurs as a result of chemical adsorption on the surface. An example can be seen in the following equation

\[
O_{2(gas)} + 2M \rightarrow 2O_{ads} \quad (5)
\]

\[
O_{ads} + V_o^- + 2e^- \rightarrow O^{2-} + M^{2+} \quad (6)
\]
Where M is a free adsorption site on a MOS and $V_o^-$ is an oxygen ion vacancy. The abstraction of two electrons from the surface of the material leads to the formation of a depletion layer on the surface as shown in Figure 1.2. The adsorption of oxygen as in the above equation modifies the defect states of the oxide surface layer to a depth of a few micrometers or less depending on the material. To use this surface layer conductivity for sensing, the operating temperature has to be high enough to facilitate gas adsorption, charge transfer and catalytic reaction but not high enough to induce bulk defect equilibration with the atmosphere.

The sensitivity and selectivity of MOS based sensors to the analyte gases depend on the chemical reactivity of the sensing oxide, the operating temperature of the device, reactions occurring on the oxide surface and the inherent conductivity of the metal oxide. Typically when sensing gases in oxygen environments with MOS devices, the operating temperature is $>300^\circ$C. At these elevated temperatures, surface oxygen species ($O^{2-}, O^-$) can exist and reactivity of these oxygen species is enhanced at elevated temperatures. The concentration/density of these oxygen ions adsorbed on the surface of MOS modulate the conductivity of the device. MOS also operate at elevated temperatures in order to have significant mobility of the charge carriers present in the material. An increase in the temperature of MOS may lead to the creation of oxygen vacancies within the material. Depending on the MOS material and its intrinsic properties, oxygen vacancies can become a source of electrons in the material making it an n-type semiconductor.

When the MOS is exposed further to an oxygen environment, oxygen atoms can adsorb to the surface of the metal oxide particles to form a depletion layer, schematically shown in Figure 1.2. A depletion layer then forms a barrier for conduction, termed as Schottky barrier at the interface of the particles, and the conduction is determined by the height of the barrier ($qV_s$). The conductivity then can be expressed by the following equation
\[
\sigma = \sigma_0 e^{-\left(\frac{q\Phi_s}{kT}\right)}
\] (7)

1.4. Optimizing Metal Oxide Gas Sensors

A variety of materials and synthesis methods have been reported for the development of MOS gas sensors [36]. These methods are focused on improving device to device reliability lowering cost, energy requirements, and improving selectivity and sensitivity.[37]

1.4.1. Sensing Platform Orientation

In the optimization on MOS gas sensing technologies the orientation of the sensing platform have been shown to play an important role. The sensing platform can be modified by varying the type, size, position of the electrode and the spacing between the electrodes relative to the thickness of the sensing layer [38-40]. Examples of the sensing platforms can be seen in Figure 1.4. The electrodes can be placed on the top, bottom and sides of the sensing layer. The electrodes can be interdigitated or two parallel planar electrodes. In some instances where the electrodes are involved in the sensing, electrodes on the top typically give the highest sensitivity. This is due to the increased exposure of the electrodes for surface catalytic reactions, while if placed on the bottom the electrodes may have better selectivity.

1.4.2. Lowering Temperature for Gas Sensing by Materials fabrication

The fabrication of MOS devices for low temperature gas sensing requires optimization of particle size, addition of catalysts both metal and metal oxide, and controlling morphology [41].

1.4.3. Lowering Temperature for Gas Sensing by Control of Particle Size

The control of particle size of MOS has been explored using methods such as sputtering [42], solgel chemistry [43], thin layer deposition techniques, screen printing [44], ink jet printing [45]
and chemical vapor deposition [46] of micro/nano-meter thin layers of MOS. Research has also involved the development of compact layers and porous layers. The thickness of the films or particle size used in gas sensing is important due to the level of depletion of the surface of the sensing material. Thus the ratio between the thickness of MOS layer and the Debye length ($\lambda_D$) is relevant. In a MOS with a crystal size of D, each particle has an electron depleted surface layer (space charge layer) of length $\lambda_D$. The thickness of this layer is influenced by the strength of oxygen chemisorption. If the particle size of the material is less than twice that of the Debye length ($2\lambda_D$), the entire particle is depleted of electrons, thus the sensitivity to an analyte gas would be dependent on the size of the MOS particle. If the MOS particle size is larger than twice that of the Debye length ($2\lambda_D$), the potential barrier at the grain boundary becomes a major factor in determining the overall resistance of the film in response to an analyte gas. Then at conditions where the particle size of the MOS is less than $2\lambda_D$ the resistance of the particles controls the resistivity of the materials to analyte gases. Hence depending on the application, the appropriate particle size is made for the optimal sensitivity to the analyte gases.

1.4.4. Lowering Temperature for Gas Sensing by Additives in Metal Oxide Semiconductor Sensors

Numerous noble metals have been studied as heterogeneous catalysts for gas combustion reactions. Gold (Au) and platinum (Pt) are the most commonly used catalysts. It has been shown that these noble metals facilitate oxidation reactions. The role of Au can involve the nanoparticle as well as involve the support. In the instance where only the gold is involved, carbon monoxide can be activated by particles consisting of $\text{Au}^0$, $\text{Au}^1\text{-OH}$ or $\text{Au}^{\text{III}}$ or combinations of these species [47]. Mechanisms involving the support which are more likely for MOS sensors may involve interfacial reactions between the carbon monoxide adsorbed on the Au nanoparticles and the
coordinatively unsaturated oxygen sites on the MOS support. Table 1.1 lists some examples of MOS metal composites for the sensing of CO such as Au-GsAs, Au-CoOOH, Au-SnO$_2$/CNT/, Au-ZnO and for NO sensing Au-WO$_3$ in Table 1.2. Platinum is also commonly used and some examples are also found in Table 1.1 Pt-SnO$_2$, Nafion-Pt in CO sensing applications and Pt-Pd/Si/Al or Pt-Pd/ WO$_3$/p-Si/Al in Table 1.2 for NO sensing.

1.4.5. Lowering Temperature for Gas Sensing by Control of Crystal Defects

The level of crystallinity of a given MOS has an important contribution to the number of defects present in the structure of the MOS [48]. The overall concentration of defects present in a given MOS crystal structure can affect the sensitivity of metal oxide gas sensor. The defects can be preserved by doping the metal oxides or heating to elevated temperatures to increase the concentration and mobility of the charge carriers.

1.5. Sensing Combustible Gases

The topic of this thesis is related to resistive gas sensors, for CO and NO. A brief background is provided regarding the reported studies for CO and NO sensing.

1.5.1. Need for carbon monoxide sensors

Carbon monoxide is an odorless, colorless, highly toxic gas which is produced from incomplete combustion processes. For methane oxidation, the reaction can be written as follows

$$2\text{CH}_4 + 3\text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2\text{O} \ (8)$$

Outdoor exposure to carbon monoxide can occur from vehicle emissions. Carbon monoxide exposure also occurs with wildfires, cooking, heating with gas, kerosene, firewood and smoking tobacco products. Carbon monoxide is a very lethal gas with few signs of poisoning and lack of
early warning. Carbon monoxide enters the blood stream through the lungs and binds to hemoglobin in the blood (Hb), the body’s oxygen carrier to form carboxyhemoglobin (COHb). This then reduces the amount of oxygen transported by the blood to the body’s organs and tissues. Tissue damage then occurs from local hypoxia. It has been noted that ambient exposures that produce 5-10% COHb (10-70 ppm CO) concentrations in the blood induce decreased function in normal body processes. Exposure to carbon monoxide should not exceed 35 ppm in a 1 hr period and 9 ppm over an 8 hr period. Several thousand people die worldwide every year from carbon monoxide poisoning.

Carbon monoxide sensors are also needed to measure the efficiency of industrial combustion processes. CO levels are indicative of poor oxygen use during combustion and can lead to considerable losses in efficiency in plants and processes.

1.5.1.1. CO sensors

Table 1.1 shows a summary of the reported low temperature carbon monoxide sensors. Each of these devices show promise but have limitations leaving room for improvement by the development of novel low energy requirement devices. Figure 1.5-Figure 1.8 show examples of the sensor designs used for the CO sensing at low temperatures.

1.5.1.1.1. Schottky-FET-Transistor

A Schottky junction made of Au/porous-GaAs [16] is used for sensing 100-300 ppm CO and NO at different temperatures. The device shows good selectivity and is more sensitive to CO than NO and shows little interferences from oxygen, hydrogen or nitrogen. The response times recorded are 0.1s and 8 mins for the recovery time for both gases. Another earlier example is ITO/n-GaAs Schottky [17] contact used to detect CO. The changes in barrier height of the diode sensor is proposed to occur by the interaction of CO with the ITO which gives a better response
than on gold. This study only looked at 1000 ppm CO. Heme on carbon nanotubes [15] have also been investigated as FET for the detection of CO at room temperature. The best sensor signal is obtained with an integrated system of thiolated heme-modified chromium-single walled nanotube network FET. This device detects as low as 4.9 ppm CO but only in nitrogen and shows a large interference to oxygen. An all carbon nanotube device [49] with a similar architecture shows similar response to 4.9 ppm CO but also shows a change in the drain current with exposure to 2.3 ppm NO₂ and 5.1 ppm NO in nitrogen. A zinc doped In₂O₃ nanowire field effect transistor [13] detects CO at 1-5 ppm.

1.5.1.1.2. SAW Devices

Polyaniline/In₂O₃ nanofibers [8] were drop cast onto the surface of a SAW transducer. This sensitive layer is used to detect 60-100 ppm carbon monoxide at room temperature in air. This device is also sensitive to H₂ in the range 0.06-1% and NO₂ in the range 510 ppb -2.12 ppm. The sensor shows signs of lack of long term stability and also does not recover after exposure to NO₂ due to poisoning.

1.5.1.1.3. Amperometric Devices

A dry and wet Nafion sensor [50] was used to detect 100-500 ppm CO in air. Both the wet and dry sensor showed good sensitivity to CO in the order of 3-7nA ppm⁻¹ with a detection limit of 0.2-0.8 ppm and response times between 20-90 seconds. Overall the wet sensor proves to be the better device with a longer lifetime of over a year although there is a need for a water reservoir. A proton conductor antimonic acid (Sb₂O₅.H₂O) is coupled with platinum loaded tin oxide (SnO₂) and tungsten oxide (WO₃) electrodes for carbon monoxide detection at room temperature. The device does not show interference to reducing gases such as methane, propane, isobutane and ethanol but gives a strong signal to hydrogen gas in the range 1300 ppm -2%.
1.5.1.1.4. Capacitive Devices

A device is made with Nafion as a solid polymer [51] electrolyte and the impedance characteristics are monitored on exposure to carbon monoxide at room temperature. The Nyquist plots showed a flattened semi-circle at high frequencies and the origin of a large semi-circle at lower frequencies which is responsive to 100-1000 ppm CO at 60% relative humidity. No other gases were investigated in this study. Carbon monoxide is also detected in hydrogen for fuel cell applications. The sensor involves an electrochemical cell with Nafion electrolyte, platinum (Pt) and ruthenium (Ru) electrodes [52]. This device works based on the differential poisoning of CO on the Pt or Ru electrodes. The device detects 10-200 ppm of CO and shows improvement with increasing the device temperature. Poisoning of the electrodes eventually affects the reversibility of the sensor which limits the long term stability of the device.

1.5.1.1.5. Resistive Devices

Multiple types of resistive gas sensors exist. These devices can be made of conducting polymeric materials, metal oxides, catalysts or a mixture of any of these. Researchers have shown that polyaniline mixed with materials such as zeolite [20], In$_2$O$_3$ [8], TiO$_2$ [10], polypyrrole-ferrocene [21] can detect CO concentrations from 16-1000 ppm at room temperature. The most common drawback of these devices is the lack of selectivity. These sensors are prone to give false positive signals to gases such as hydrogen, ammonia (NH$_3$) and moisture. Gas sensing with polymers [53] is typically conducted in controlled environments that are either oxygen free or in controlled humidity which limits the application of such devices. Another class of resistive based devices include semiconducting metal oxides, these may include semiconductors such as TiO$_2$ [54], SnO$_2$, Au-SnO$_2$, Pt-SnO$_2$ [55-57], Mn-Fe$_3$O$_4$ [25]. These devices typically operate at temperatures $>200^\circ$C. There are some recent examples of low temperature operating sensors
based on cobalt oxides, gold and single walled carbon nanotubes added to CoOOH-WO₃ composites. They are reported for the detection of 1-1000ppm CO, Co₃O₄, Au-CoOOH [27,58,59] at 80°C and Au-ZnO [28], iron oxide [60] at 25°C.

1.5.1.1.6. I-V coupled Devices

A porous silicon [61] thin film made by electrochemical anodization of Si substrates, exhibited a change in the resistance by an order of magnitude in the presence of CO (which is assumed to be 100%). Tin oxide /multi wall-carbon nanotube composite nanofibers detect CO 50-500 ppm [62] with changes observed in the slope of the I-V curves. No other gases were tested for interference effects and cross sensitivity.

1.5.2. Need for NOx sensors

NOx is a serious pollutant in today’s environment due to industrialization, about half of all the NOx in the environment is due to fossil fuel combustion emissions from motor vehicles. The right combination of sunlight, concentration of NOx (ppb-ppt) and temperature leads to significant smog formation. NOx has many harmful effects, such as respiratory irritation, choking, headaches, dizziness, nausea, vomiting dyspnea, burning sensation in the chest, sleeplessness, restlessness, lassitude and heart palpitations. While NOx in the body, it plays key roles in the regulation of blood flow, heart rate [63], wound healing [64], nerve [65] signals and immune function [66,67]. The detection of NOx levels in breath has also been recently shown to be a possible diagnostic for pulmonary hypertension and asthma [68]. Table 1.2 provides a summary of low temperature NOₓ sensors.

1.5.2.1. NO Sensors
Table 1.2 shows a summary of the state of the art low temperature NOx sensors. Each of these devices show promise but have limitations leaving room for improvement by the development of novel low energy requirement devices. Figure 1.5-Figure 1.8 show possible examples of sensor designs used for the NOx sensing at low temperatures.

1.5.2.1.1. Schottky –FET-Transistors

High temperature semiconductors [18] have been applied to gas sensing by incorporating them into FET devices. Cuprates $Y_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ and $(\text{Bi}:\text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ are selective to NH$_3$, H$_2$, CO, CO$_2$, NO, NO$_2$, and hydrocarbon gases in a nitrogen atmosphere. The best selectivity is achieved at room temperature where the device detects only NO$_2$ and NH$_3$. An organic [14] based FET shows sensitivity to both NO and NO$_2$ with a sensitivity to 250 ppb of NO$_2$. A silicon Schottky diode structure [69] is shown to detect NO$_x$ at room temperature with a detectable range of 5-22 ppm for NO$_2$, 50-250 ppm NO. The porosity of the materials enhances the sensitivity of the devices but also increased the response times of the device. Stability and drift of the baseline was not observed to be a problem in this device. Varistor-type gas sensor made of micro p-n junctions [70] of SnO$_2$ and Cr$_2$O$_3$ detect NO$_x$ at 200-600°C in the range of 20-100 ppm. The amount of Cr$_2$O$_3$ varied the sensitivity to each of the gases and the particle size reduction also improved the sensitivity of the device.

1.5.2.1.2. SAW Devices

Polymeric organic films when coated on SAW devices have shown good sensing performance for NO and NO$_2$, these devices also respond to NH$_3$, H$_2$O, CO, CH$_4$, SO$_2$ and H$_2$S and organic vapors. These devices detect 1000-4000 ppm NO and 1-10 ppm NO$_2$ in nitrogen atmosphere only.

1.5.2.1.3. Resistive Devices
Palladium (Pd), platinum (Pt), gold (Au) on tungsten oxide (WO$_3$) thin films [71] show good sensitivity to 20-440 ppm NO and 1-10 ppm NO$_2$ in the temperature range of 100-200°C. The doping of the WO$_3$ improves the sensor selectivity over un-doped WO$_3$ and does not respond to CO, CH$_4$, H$_2$S, SO$_2$, NH$_3$ and hydrogen gas. Gas sensors based on indium oxide (In$_2$O$_3$) and tungsten oxide (WO$_3$) [31] nanowires have shown good selectivity for NOx gases. The detection range is between 0.1 ppm and 100 ppm for NO, NO$_2$ and N$_2$O. The lowest operating temperature is 125°C and the sensitivity of the gases to each of the films is dependent on the operating temperature. Tungsten oxide [32] and tungsten oxide composites [33] show high temperature (>150°C) sensitivity to NO in air. Multi-walled carbon nanotubes [22,23,72] have also shown promise as NOx sensor and operate from 25-150°C. These devices operate in inert atmospheres and detect concentrations down to 1 ppm NO with interferences from NO$_2$.

1.6. Low Temperature Gas Sensors

Although the carbon monoxide sensors shown in Table 1.1 operate at room temperature they each has limitations like in the case of the Schottky-FET-Transistor devices they only operate in oxygen free environments which is not practical for an ambient carbon monoxide sensor. The SAW devices are not stable over long periods and the surface is prone to fouling. Issues on the amperometric devices are the humidity requirement and non-selective to other reducing gases. The capacitive devices do not show good sensitivity or the promise of selectivity over other reducing gases. The resistive devices having the advantage for miniaturizability, show good sensitivity to carbon monoxide at room temperature but show large interferences due to other reducing gases, some require special environmental considerations such as fixed humidity, vacuum and oxygen free environments. These devices in general operate at room temperature but
have an optimum working range impractical for an ambient carbon monoxide sensor with the operating temperature being either above the specified requirement or the detectable range being above lethal doses for carbon monoxide. This provides an opportunity for the development of a device that takes into account all the specifications and requirements of an ambient carbon monoxide sensor such as miniaturizability, selectivity to carbon monoxide, operational at 25°C, detection range of 10-1000 ppm carbon monoxide in air, humidity resistance and long term stability.

The examples in Table 1.2 show examples of sensors and devices of the existing low temperature NO and NO₂ sensors. The complexity in the Schottky-FET-Transistor devices limits their application due to the difficulty in miniaturizing the devices. Their cross sensitivity to NO₂ is also considered an issue in selecting these as ambient sensor for NO as they respond better to NO₂ than NO. The SAW device is only operational in a nitrogen atmosphere and shows greater sensitivity to other gases such as ammonia, carbon monoxide, methane and NO₂. The resistive devices on the other hand have different positive and negative factors. Some have shown good room temperature performance but still have better response to NO₂. Some improvements in lowering detection limits lead to sacrifices in the operational temperature without any improvement in selectivity. These devices show the state of the art in low temperature NO detection and the hurdles and limitations still present in the development of selective devices, providing an opportunity for further work and development of an optimal device for low temperature detection of NO.

The subject matter of this dissertation involves a new class of resistive based electrochemical gas sensors based on RuOₓ(OH)ᵧ and V₂O₅. Electrochemical measurements are rapidly and readily made by simple electronics, and integration into electronic devices is potentially straightforward.
In illustrating the potential of a new class of metal oxide gas sensors, carbon monoxide and nitric oxide will be used.

The use of conducting metal oxide has not been studied and thus forms the subject matter of this dissertation as a new class of materials for gas sensing applications. The fabrication of the devices, their synthesis, performance and sensing mechanisms will be discussed.
References


47. Bond, G.C.; Louis, C.; Thompson, D.T. *Catalysis by Gold.*; Imperial College Press, **2006**.


Table 1.1 Summary of low temperature carbon monoxide gas sensors

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>Sensing Principle</th>
<th>Measurement Technique</th>
<th>Sensitivity and Selectivity</th>
<th>Minimum Working Temperature</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Schottky-FET-Transistor Devices</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Au/porous GaAs[16]</td>
<td>Changing Schottky barrier</td>
<td>I-V measurement Bias voltage, measure I</td>
<td>seconds</td>
<td>RT better at 100 °C</td>
<td>Miniaturizable Only tested with N₂ background</td>
</tr>
<tr>
<td>2. ITO/GaAs[17]</td>
<td>- Fe in heme interacts with CO</td>
<td>Change in drain current</td>
<td>seconds</td>
<td>RT</td>
<td>Miniaturizable Only tested with N₂ background</td>
</tr>
<tr>
<td>3. CNT-FET[15]</td>
<td>Interaction of CO with SWNT COOH</td>
<td>Change in drain current</td>
<td>minutes</td>
<td>RT</td>
<td>Miniaturizable Problems in air</td>
</tr>
<tr>
<td>4. SWNT-transistors[15,49]</td>
<td>Change in conductivity of the nanowire upon Zn-doping</td>
<td>Change in drain current</td>
<td>Seconds</td>
<td>RT 1-5ppm</td>
<td>Sensitive to NO, NO₂ Oxygen free environment</td>
</tr>
<tr>
<td><strong>SAW Devices</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Polyaniline-In₂O₃[8]</td>
<td>Conductivity change coupled with SAW device</td>
<td>Frequency</td>
<td>seconds</td>
<td>RT</td>
<td>Long term stability an issue</td>
</tr>
<tr>
<td><strong>Amperometric Devices</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Nafion-electrochemical cell[50]</td>
<td>fuel cell principle</td>
<td>Amperometric</td>
<td>minutes</td>
<td>RT</td>
<td>Needs H₂O reservoir</td>
</tr>
<tr>
<td>8. Sb₂O₃.2H₂O[73]</td>
<td>Proton conductor</td>
<td>Amperometric</td>
<td>minutes</td>
<td>1000ppm RT</td>
<td>Similar signal to H₂</td>
</tr>
<tr>
<td><strong>Capacitive Devices</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Nafion-Pt cloth[51]</td>
<td>Changing capacitance, kinetics of charge transfer</td>
<td>Impedance spectroscopy</td>
<td>no data shown</td>
<td>RT</td>
<td>Complete sensor behavior not shown</td>
</tr>
<tr>
<td>10. Nafion-Pt/Pt-Ru[52]</td>
<td>fuel cell principle</td>
<td>Exploiting differential poisoning of electrodes</td>
<td>minutes</td>
<td>70% CO</td>
<td>Impractical for current application</td>
</tr>
<tr>
<td><strong>Resistive Devices</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. Polyaniline zeolite[20]</td>
<td>Polyaniline is sensing</td>
<td>Resistance</td>
<td>minutes</td>
<td>RT 16ppm</td>
<td>No traces shown</td>
</tr>
</tbody>
</table>

Continued
Continued Table 1.1

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>CO oxidation</th>
<th>Behavior</th>
<th>Sensitivity</th>
<th>Baseline Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.</td>
<td>Pt-SnO$_2$[24]</td>
<td>CO oxidation</td>
<td>Resistive</td>
<td>Minutes</td>
<td>RT 300ppm</td>
</tr>
<tr>
<td>15.</td>
<td>Au-Fe$_2$O$_3$[25]</td>
<td>CO oxidation</td>
<td>Resistive</td>
<td>Minutes</td>
<td>200ppm at 200°C</td>
</tr>
<tr>
<td>16.</td>
<td>Mn-Fe$_3$O$_4$ [60]</td>
<td></td>
<td>Resistive</td>
<td>Seconds</td>
<td>20mTorr RT</td>
</tr>
<tr>
<td>17.</td>
<td>Au/CoOOH, Au/Co$_3$O$_4$[27]</td>
<td>CO oxidation</td>
<td>Resistance $10^7$ Ω, p-type</td>
<td>minutes</td>
<td>80 °C</td>
</tr>
<tr>
<td>18.</td>
<td>Au-ZnO[28]</td>
<td>CO oxidation</td>
<td>Resistive</td>
<td>Seconds</td>
<td>100ppm</td>
</tr>
<tr>
<td>19.</td>
<td>ZnO nanowires[29]</td>
<td>CO oxidation</td>
<td>Resistive</td>
<td>Minutes</td>
<td>120ppb</td>
</tr>
<tr>
<td>20.</td>
<td>Co$_3$O$_4$[59]</td>
<td>CO oxidation</td>
<td>Measure V with applied V</td>
<td>Seconds</td>
<td>RT 4ppm CO</td>
</tr>
<tr>
<td>21.</td>
<td>SnO$_2$/CNT[56]</td>
<td>CO oxidation</td>
<td>I measurement with applied V</td>
<td></td>
<td>RT 47ppm</td>
</tr>
<tr>
<td>22.</td>
<td>Pt-SnO$_2$[57]</td>
<td>CO oxidation</td>
<td>Measure V with applied V</td>
<td>minutes</td>
<td>5000ppm</td>
</tr>
<tr>
<td>23.</td>
<td>Au-SnO$_2$ on CNT[62]</td>
<td>CO oxidation</td>
<td>Bias voltage, measure I</td>
<td>minutes</td>
<td>RT 500ppm</td>
</tr>
</tbody>
</table>

**I-V coupled Devices**

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>I-V measurement</th>
<th>Sensitivity</th>
<th>Baseline Conditions</th>
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</thead>
<tbody>
<tr>
<td>24.</td>
<td>Porous Silicon[61]</td>
<td>I-V measurement</td>
<td>Minutes</td>
<td>RT No CO concentration</td>
</tr>
<tr>
<td>25.</td>
<td>CNT on Co$_3$O$_4$-SnO$_2$[74]</td>
<td>Adsorption/Desorption</td>
<td>Measure V with applied V</td>
<td>Seconds</td>
</tr>
</tbody>
</table>
Table 1.2 Summary of low temperature NO and NO₂ sensors

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>Sensing Principle</th>
<th>Measurement Technique</th>
<th>Sensitivity and Selectivity</th>
<th>Minimum Working Temperature</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>Schottky-FET-Transistor Devices</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Y₁Ba₂Cu₃O₇-x and (Bi: Pb)₂Sr₂Ca₂Cu₃O₁₀[18]</td>
<td>Capacitively controlled FET</td>
<td>Change in gate voltage due to work function of gas</td>
<td>Minutes</td>
<td>1000ppm 18°C</td>
<td>Not selective shows better sensitivity to NH₃ H₂ CO CO₂ and NO₂</td>
</tr>
<tr>
<td>2. Decyl functionalized teranthylene-ethynylene[14]</td>
<td>Organic FET</td>
<td>Change in gate voltage</td>
<td>Minutes</td>
<td>5ppm in N₂</td>
<td>Higher sensitivity to NO₂</td>
</tr>
<tr>
<td>3. Pt–Pd/Si/Al[69]</td>
<td>Diode</td>
<td>Current</td>
<td>Minutes</td>
<td>23°C 50ppm</td>
<td>Higher sensitivity for NO₂</td>
</tr>
<tr>
<td>4. Pd-Pt/WO₃/p-Si/Al[75]</td>
<td>Diode</td>
<td>Current</td>
<td>Minutes</td>
<td>23°C 50ppm</td>
<td></td>
</tr>
<tr>
<td>5. SnO₂ + 5.0 wt% Cr₂O₃[70]</td>
<td>P-n junction</td>
<td>Chemisorption of NO</td>
<td>20ppm in Air 200-600°C</td>
<td>NO₂ interference</td>
<td></td>
</tr>
<tr>
<td>SAW Devices</td>
<td></td>
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<tr>
<td>6. Organic and Organometallic poly-yenes[9]</td>
<td>Surface Acoustic (SAW) and Surface transverse wave (STW)</td>
<td>Minutes</td>
<td>80-4000ppm in N₂</td>
<td>Better sensitivity to NO₂ , NH₃ , H₂O , CO, CH₄ SO₂ , H₂S</td>
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<td>Resistive Devices</td>
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<td>8. In₂O₃ and WO₃ nanowires[31]</td>
<td>Resistive</td>
<td>Seconds</td>
<td>10ppm 125°C</td>
<td>NO₂ and N₂O have the same sensitivity</td>
<td></td>
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<tr>
<td>9. WO₃[32]</td>
<td>Resistive</td>
<td>Minutes</td>
<td>250°C in Air 100ppm</td>
<td>NO₂ stronger signal</td>
<td></td>
</tr>
<tr>
<td>10. WO₃-Bi₂O₃[33]</td>
<td>Resistive</td>
<td>Minutes</td>
<td>150°C in Air 2-300ppm</td>
<td>No interference studies</td>
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<tr>
<td>11. MWCNT laser irradiated[72]</td>
<td>Resistive</td>
<td>Minutes</td>
<td>2ppm in N$_2$ 150°C</td>
<td>No interference studies</td>
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<td>12. MWCNT[22]</td>
<td>Resistive</td>
<td>Minutes</td>
<td>2-10ppm 25°C</td>
<td>NO$_2$ stronger response</td>
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<td>13. Carbonyl functionalized MWCNT and SWCNTS[23]</td>
<td>Resistive</td>
<td>Interaction of NO and CNT</td>
<td>Minutes</td>
<td>1ppm in Ar or Air 1ppm</td>
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Figure 1.1 Different sensor platforms for metal oxide semiconductor sensors from reference [76].
Figure 1.2. Two metal oxide semiconductor particles showing the formation of the surface depletion layer upon exposure to oxygen.
Figure 1.3. Interaction of two MOS particles forming depletion layers when exposed to (a) oxidizing gas oxygen (b) reducing gas carbon monoxide.
Figure 1.4. Different electrode constructs with metal oxide semiconductor (MOS) deposited. Design is similar in resistive, capacitive and IV coupled devices.
Figure 1.5. Field effect-transistor devices for gas sensing based on reference [15].
Figure 1.6. Schematic of a surface acoustic wave device for gas sensing applications.
Figure 1.7 Amperometric CO sensor from reference [50]. (a) Top view (b) Sensor cross section (C.E., counter electrode, W.E., working electrode and R.E., reference electrode).
Figure 1.8. Potentiometric Sensor.
CHAPTER 2: HYDROUS RUTHENIUM OXIDE AS A PLATFORM FOR CARBON MONOXIDE SENSING AT AMBIENT CONDITIONS

2.1. Introduction

Ruthenium oxide (RuO$_2$) is an important technological material. In particular, its electrical properties are dependent on its structure, with the room temperature conductivity of single crystalline RuO$_2$ reported as high as $\sim 10^4$ S/cm [1], poly crystalline RuO$_2$ $\sim 10^3$ S/cm [2] and amorphous hydrous RuO$_2$ is $\sim 1$ S/cm [3]. In its crystalline form, RuO$_2$ adopts a rutile structure, and exhibits metallic-like conductivity. The crystalline form of RuO$_2$ is used in the electronics industry as electrodes in integrated circuits [4], and also as electrodes for industrial production of hydrogen, chlorine and oxygen [5,6]. The catalysis applications of RuO$_2$ include water splitting [7,8], oxidation of methanol and ethanol [9] and carbon monoxide oxidation [10].

The hydrated form of ruthenium oxide, RuO$_x$(OH)$_y$ is an amorphous material and finds use in the power industry as supercapacitors [11,12]. The supercapacitor performance of RuO$_x$(OH)$_y$ stems from its ability to reversibly incorporate protons and electrons, as shown below [11,12]:

$$\text{RuO}_x(\text{OH})_y + \delta \text{H}^+ + \delta \text{e}^- \leftrightarrow \text{RuO}_{x-\delta}(\text{OH})_{y+\delta} \quad (1)$$

Several studies have discussed the structure of RuO$_x$(OH)$_y$ [11-13]. The picture that emerges is that the nanoparticles present in RuO$_x$(OH)$_y$ consist of disordered arrangements of RuO$_6$ chains, capped off by OH groups. Within the grains, conductivity is considered to be primarily metallic-like arising from the d-band structure. Conduction involves electron hopping between the particles, and this process is dependent on the size of the particle. Optimization of the supercapacitor performance of RuO$_x$(OH)$_y$ has focused on studies of the interfacial electron
transfer between the nanoparticles, and control of the microstructure [13]. For example, a hydrated form of mesoporous RuO$_2$ was reported to have excellent capacitive behavior [14]. Hydrous amorphous ruthenium oxide is also a carbon monoxide oxidation catalyst under ambient conditions. However, the catalytic activity is strongly dependent on the thermal history of the samples, and diminishes as the material is heated [15].

In this chapter, we focus on the electronic conductivity of hydrated amorphous ruthenium oxide and changes thereof in the presence of carbon monoxide. Using information from infrared spectroscopy, we propose a mechanism for the observed changes in electrical properties. The change in conductivity with CO at room temperature was also exploited to develop an ambient CO monitor. There is need for low power, solid state, minaiturizable CO sensors, and to the best of our knowledge, this study reports the first example of use of hydrated amorphous ruthenium oxide as an ambient chemoresisitive CO sensor. Most semiconducting metal oxides such as TiO$_2$ [16,17], polyanline-TiO$_2$ [18], Au-Co$_3$O$_4$ [19], SnO$_2$ [20], detect CO at high temperatures. Modifications of metal oxides by addition of noble metals as in Pt-SnO$_2$ [21] and Au-ZnO [22] can lower the temperature of operation. Metallic RuO$_2$ is used as a gate material in field effect sensor devices [23].

**2.2. Experimental**

2.2.1. Materials Synthesis

2.2.1.1. *Wet precipitation*

Hydrated ruthenium oxide (RuO$_x$(OH)$_y$), was prepared by a precipitation method [24]. To a stirred 0.1M aqueous solution of ruthenium chloride (RuCl$_3$.xH$_2$O Sigma Aldrich), 0.3M sodium hydroxide (Mallinckrodt 98.7%) solution was added drop-wise until pH 7. The resulting
precipitate was washed several times until chloride free (tested with AgNO₃), and dried in air at room temperature. Heat treatment of RuOₓ(OH)ᵧ was carried out at 100°C, 200°C, 300°C, 400°C, 500°C and 600°C for 10 hr each. The resulting powders were crushed in an agate mortar and pestle for 5 min and used for all further experiments.

2.2.1.2.  

Supercritical drying

A Tousimis, Samdri-PVT-3D super critical dryer (SCD) was used for the experiments. Absolute ethanol (200 proof) from Fisher Scientific, for these experiments was distilled over calcium hydride for two days before use. RuOₓ(OH)ᵧ was synthesized by wet precipitation as mentioned above. The resulting gelatinous paste was exchanged with dry ethanol and used for the solvent exchange in the super critical drying experiments. Equal volumes of RuOₓ(OH)ᵧ paste is applied to the surface of two gold interdigitated electrodes and one of the devices was put into the drying instrument. The drying cycle took about 30 min. The sample was left to dwell at supercritical conditions for a minimum of 10 min before the gases were slowly released from the chamber.

The sensors obtained were used for gas sensing experiments and compared with similarly made devices dried in air or exchanged in water. The devices were exposed to 1000 ppm carbon monoxide in air at 100 ccm/min.

2.2.2.  

Materials Characterization

Thermogravimetric analysis (TGA) experiments were carried out with Perkin Elmer TGA 7, with a Thermal Analysis Controller, TAC 7/DX. A ramp rate of 10°C/min in nitrogen gas flow of 40 cc/min was used. A Rigaku Geigerflex X-ray diffractometer with Ni-filtered Cu Kα radiation was used for powder diffraction measurements. A Tecnai F20 with field emission 200kV STEM and X-TWIN lens was used to elucidate the microstructure and particle size. The Kratos AXIS
Ultra X-ray photoelectron spectrometer (XPS) with an Al source was used for all XPS analysis. A 13 kV voltage with a 10 mA current and pass energy of 20 eV at 0.1 eV resolution was used. CasaXPS Version 2.3.15 software was used for the deconvolution of the XPS data. A Shirley background was used for all data processing. The binding energies were calibrated relative to the Na 1s peak at 1072 eV.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analysis was carried out in a controlled environment cell (Pike Technologies) with a ZnSe window in a Perkin Elmer Spec400 spectrometer. Samples of 25 wt% of RuO₄(OH)ₓ dispersed in spectral grade KBr (Pike Technologies) was used for each experiment. Certified mixtures of CO, 2000 ppm in N₂ (Praxair), 100% CO₂ (Praxair) and 21% oxygen in argon (Praxair) were used with gas flow rates of 60 cc/min. Scans were collected in the range 4000-850 cm⁻¹ with a resolution of 4 cm⁻¹. All spectral subtractions were done with the Spectrum 6.3.1 software (Perkin Elmer). The subtraction factor was varied between 0.932 and 1.000 until the νCH stretching vibrations peaks at 2800-2950 cm⁻¹ were minimized. A mercury cadmium telluride (MCT) detector was used for the IR measurements.

2.2.3. Resistance Measurements

Alumina substrates (10 mm X 10 mm) with interdigitated gold lines of 0.25 mm spacing were obtained from Case Western Reserve University Electronics Design Center. Gold lead wires (Alfa Aesar, 99.99%) were connected with gold paste (Heraeus). The electrodes were heat treated at 600°C for 3 hours in order to remove organic binders from the gold paste. The RuO₄(OH)ₓ particles were suspended in water (5% by weight) by sonication for 1 hr. The
suspension was drop coated onto the electrodes and allowed to dry in air for 4-6 hr. The sensor fabrication and electrodes are shown in Figure 2.1.

All tests were done with a quartz tube housed in a temperature programmable furnace (Lindberg Blue, TF55035A). Measurement protocol consisted of flowing various volumes of certified mixtures of carbon monoxide 2000 ppm in N₂ (Praxair), 50% oxygen in N₂ (Praxair) and nitrogen (Praxair) over the devices to give 250-1000 ppm CO in 21% oxygen, balanced with nitrogen in order to keep the flow rate constant. Certified premixed carbon dioxide 2000 ppm in nitrogen (Praxair), methane 2000 ppm in nitrogen (Praxair), propane 2000 ppm in nitrogen (Praxair), and ammonia 300 ppm in nitrogen (Praxair) were used. Gas concentrations were varied by varying the flow of each gas with a Sierra Side-Trak® model 840 analog gas mass flow controller, controlled by a National instruments card (NI-6703) and operated by a Labview program. All mass flow controllers were calibrated with each gas used in the experiment within +/-5 sccm. The gases were calibrated with a Fisher Scientific digital flow meter model 520. Resistance measurements were made with a HP34970A at a scan rate of 0.1 Hz. Tests were carried out at 25°C with a gas flow rate of 100 cc/min for all experiments. The experimental set up for all gas sensing experiments is shown in Figure 2.2.

2.3. Results

2.3.1. Synthesis and Characterization of RuOₓ(OH)ᵧ

As expected from earlier reports [24], a brown aqueous solution of RuCl₃.xH₂O changes to a black solution as the pH was gradually increased. When stirring was stopped at pH 7, a black solid collected at the bottom leaving a clear liquid at the top. The precipitate (RuOₓ(OH)ᵧ) was separated by centrifugation and forms the subject matter of this chapter. The weight loss upon
heating of RuO$_x$(OH)$_y$ was carried out by thermogravimetric analysis, and the data is shown in Figure 2.3a. The weight loss occurs in three stages, a moderately rapid loss until ~225°C, a gradual loss until 1125°C, followed again by a rapid loss. These stages have been described in literature as arising from water loss via loss of H$_2$O and OH groups and finally the reduction to metal beyond 1050°C [25]. Based on the TGA data shown in Figure 2.3a, a drop in mass for RuO$_x$(OH)$_y$ due to water/OH loss over the temperature range of 25-325°C is observed. A change in mass from 100% at 25°C to 78% at 325°C resulting in a ~22% change, indicates a molecular formula of RuO$_2$.2H$_2$O. Figure 2.3b shows the diffraction pattern of the as-synthesized RuO$_x$(OH)$_y$, the absence of peaks indicating that it is an amorphous material. Figure 2.3c shows a TEM image for the RuO$_x$(OH)$_y$. The primary particle size based on the analysis of ~100 particles is found to be between 20-50 nm.

X-ray Photoelectron Spectroscopy of RuO$_x$(OH)$_y$ in the O 1s and Ru 3d region is shown in Figure 2.4. Curve deconvolution of the oxygen 1s region (Figure 2.4a), results in three peaks at 528.0, 529.0 and 531.0 eV, indicating the presence of multiple oxygen species. Based on the literature assignments of O$^{2-}$ at 529.4eV, OH$^-$ at 530.8eV, and H$_2$O at 532.4eV [26], these peaks are assigned in order of increasing binding energy to Ru-O-Ru, Ru-OH and Ru-H$_2$O. However, our infrared studies discussed later show the presence of carbonates on the as-synthesized material, and carbonate oxygen can also contribute to the 531eV peak [27].

The Ru 3d region for RuO$_x$(OH)$_y$ exhibits two broad bands at ~ 280 and ~285 eV (Figure 2.4b), the intensity arising from the 3d $^5/2$ and $^3/2$ electrons. Several studies have reported the XPS of different forms of hydrated ruthenium oxide with the 3d $^5/2$ ranging from 280.4 eV to 281.2 eV and 3d $^3/2$ ranging from 284.6 eV to 285.4 eV [25,26,28-30]. There is general consensus that the peak varies depending on synthesis techniques and heat treatment conditions, but arises from a
mixture of Ru (III) and Ru(IV), resulting in the broad bands observed. In addition, the hydroxyl and oxygen functionalities surrounding the Ru also lead to broadening, and therefore makes the deconvolution of the Ru 3d region complicated. There is also contribution from the C 1s in this binding energy range. The best fit was obtained with six peaks at 279.3, 280.1, 282.1, 283.6, 284.5 and 295.7 eV. The peaks at 279.3 and 283.6 eV are assigned to hydrous Ru(III) and 280.1 and 284.5 eV to Ru(IV). Since the starting material is RuCl$_3$·xH$_2$O, we discount the formation of Ru(0) in the RuO$_x$(OH)$_y$ since treatment with base should not result in reduction. The other two peaks at 282.1 and 285.7 eV are assigned to C 1s from carbonaceous impurities and carbonate respectively [25-27], the presence of carbonate is confirmed by infrared spectroscopy.

2.3.2. Interaction of RuO$_x$(OH)$_y$ with CO

2.3.2.1. Resistance Changes

Figure 2.5 shows the changes in resistance of a thick film of RuO$_x$(OH)$_y$ upon repeated exposure to 250 ppm CO at 25°C in a background of dry 21% O$_2$ (the rest is N$_2$). There is a decrease in baseline resistance upon initiation of the measurement, and is attributed to drying of the sample. The baseline does stabilize with time. There is an increase in resistance with CO, and a decrease as the CO is turned off in the gas stream over the film. This cycle can be repeated numerous times (~100) with an average relative resistance change, $R/R_0$ ($R/R_0$, where R is the resistance in the presence of the CO and $R_0$ is the resistance in the background gas) of 2.5.

2.3.2.2. In-situ infrared spectroscopy

Diffuse reflectance infrared spectroscopy (DRIFTS) was used to monitor the surface of RuO$_x$(OH)$_y$ as O$_2$ and CO was passed over the surface. Figure 2.6a shows the infrared spectrum of the as-synthesized sample, Figure 2.6b after passing O$_2$ (21%) over the sample for 150 min, Figure 2.6c after 2000 ppm CO flown over the sample shown in Figure 2.6b for 15 min, Figure
2.6d with 21% oxygen flowing over the sample shown in Figure 2.6c for 30 min, and then the cell was closed off for 45 min. Figure 2.6e after O2 (21%) exposure for 150 min over the sample shown in Figure 2.6c and Figure 2.6f is after CO2 exposure of the sample shown in Figure 2.6b. In these spectra, there are changes observed over several regions. Figure 2.6a shows that the as-synthesized sample has bands in the carbonate (1000-1800 cm\(^{-1}\)) and hydroxyl (3600 and 1600 cm\(^{-1}\)) regions, which disappear in flowing air. The best way to visualize these changes was by taking difference spectra, which are shown in Figure 2.7. The extent of the subtraction was controlled so the intensity in the C-H stretching region was minimized. The sample treated with air (Figure 2.6b) is considered the primary control sample and is used in all the spectral subtractions. Figure 2.7b shows that after exposure to 2000 ppm CO (Figure 2.6c – Figure 2.6b), new bands at 866, 1038, 1167, 1281, 1311, 1433, 1539, 1617 and 1650 cm\(^{-1}\) are observed in the carbonate region. Bands at 1433, 1311 and 1167 cm\(^{-1}\) are assigned to monodentate carbonate, bands at 1539, 1281 cm\(^{-1}\) to bidentate carbonates and 1617, 1038 cm\(^{-1}\) to bicarbonates and summarized in Table 2.1 [31-34]. In addition, gas phase CO peaks are observed around 2150 cm\(^{-1}\). In the O-H stretching region, there is increase in intensity at 3367 cm\(^{-1}\) and loss of intensity at 3618 cm\(^{-1}\), there is also an appearance of a shoulder ~1650 cm\(^{-1}\) due to the bending mode of water. Figure 2.7c is the difference spectrum for a CO-exposed sample that was treated with flowing oxygen for 30 minutes, and then the cell was closed off (Figure 2.6d – Figure 2.6b), and bands at 1050, 1297, 1515 and 1620 cm\(^{-1}\) are observed in the carbonate/bicarbonate stretching region, and there is a loss of the monodentate carbonate peaks, and the water bending mode. In addition, chemisorbed CO bands are observed at 2003 cm\(^{-1}\), 2043 cm\(^{-1}\) and 2059 cm\(^{-1}\) and adsorbed CO\(_2\) at 2354 cm\(^{-1}\), in addition to the water band at 3426 cm\(^{-1}\). The difference spectrum between the two long-term exposed O\(_2\) samples is shown in Figure 2.7a (Figure 2.6e- Figure
2.6b), indicating that passing air over a CO-exposed sample over a longer period of time essentially removes all of the new species formed upon CO reaction. The entire cycle of O₂ and CO introduction could be repeated several times, with comparable infrared data. Figure 2.7d is the difference spectrum upon CO₂ exposure to RuOₓ(OH)ᵧ (Figure 2.6f – Figure 2.6b). Bands at 1052, 1297, 1539, 1617 cm⁻¹ are observed in the carbonate/bicarbonate region, CO₂ at 2333 cm⁻¹ and the water band at 3410 cm⁻¹.

2.3.3. Change in Properties of RuOₓ(OH)ᵧ with Heat Treatment

Samples of RuOₓ(OH)ᵧ were heated up to 600°C, and structural as well as resistivity changes were measured under ambient conditions. Figure 2.8, shows the powder diffraction pattern of the samples obtained at the various temperatures. Peaks begin to form in the sample heated to 300°C, and these peaks increase in intensity and sharpen as the heat treatment temperature is increased. The dominant peaks at 28°, 35° and 54° (2θ) correspond to the 110, 101 and 211 reflections of the rutile RuO₂ structure [25]. Correlating this observation with the TGA data in Figure 2.3a, it is clear that following the loss of water, the amorphous material is becoming crystalline. The XPS data were obtained for all the samples and the data in the Ru 3d and O 1s region for the sample heated to 600°C is shown in Figure 2.9a and Figure 2.9b. As indicated in Figure 2.9 the spectrum of RuOₓ(OH)ᵧ has multiple oxygen species Ru-OH (529.0eV) and Ru-H₂O (531.0eV) and Ru-O-Ru (528.0eV) [25]. There is an evident change in peak shape observed in the XPS spectra of the O 1s region of the heated samples (Figure 2.9b). With increasing heat treatment temperature the Ru-O-Ru peak increases and sharpens in comparison to the other peaks for the Ru-OH and Ru-H₂O components which decrease. The ratios of these peaks change with heat treatment, with increasing contributions from Ru-O-Ru with the maximum contribution for the 600°C sample.
The spectrum was fit to three peaks as observed in Figure 2.9b. In the Ru-3d region (Figure 2.9a), there is a sharpening of the Ru 3d $^5/2$ peak with heating and a shift to lower binding energies. This is a reflection of the oxidation of Ru(III) to Ru(IV) as well as the loss of hydroxides on the ruthenium [26]. For the 600°C treated sample, the Ru 3d XPS data was fit to four peaks (Figure 2.9c). The low-binding energy doublet (281.2, 285.4 eV) is assigned to a screened final state and the high-binding energy doublets (282.8, 286.0 eV) to the unscreened final state, both for Ru(IV) typical of crystalline RuO$_2$ [30]. Figure 2.10a shows the change in resistance of the various heat treated samples upon exposure to 500, 250 and 1000 ppm of CO. The relative changes in resistance ($R/R_o$, where $R$ is the resistance in the presence of the CO and $R_o$ is the resistance in the background gas) is plotted as a function of concentration. The slopes of the line are an indication of the sensitivity of the device and are shown in Figure 2.10b. Clearly, the resistance change diminishes with heat treatment with relative resistance change of 50% for 25°C, 29% for 100°C, 13% for 200°C, 7% for 300°C, and is not observable beyond 400°C.

2.3.4. CO Sensing Potential of RuO$_x$(OH)$_y$ under Ambient Conditions

The change in resistance of RuO$_x$(OH)$_y$ with CO provides an opportunity for developing a solid state electrochemical ambient CO sensor. Multiple devices were made with RuO$_x$(OH)$_y$ and tested in parallel at 25°C. Figure 2.11 shows the response of three devices to 1000, 500, 250, 1000 ppm CO in an air background. Response times and recovery times for the 1000 ppm CO were calculated to be 6 and 11 minutes (time taken to reach 90% of the steady state signal). The inset in Figure 2.11 shows the response with 32 ppm CO over a 12-hour period, and the response appears to be stable. We did notice that beyond 16 hours, a gradual decrease in signal is observed. Figure 2.12 depicts the normalized resistance ($R/R_o$) to 2000 ppm CO$_2$, 1000 ppm
methane and propane, 150 ppm ammonia, 15 ppm NO and NO₂, indicating that the device is selective towards CO.

2.3.5. Device Optimization

In order to optimize this sensor, a strategy to increase the effective surface area of the RuO₃(OH)ₓ by super critical drying (SCD) was considered. The increase in surface area is expected to increase the sensitivity of the sensor since the carbon monoxide interacted with the surface of the material. Supercritical drying was first used by S S Kistler in the 1930’s [35] as a method to dry gels and retain the integrity of the gel which would collapse when dried by conventional methods. Super critical fluids have found use in applications such as materials processing of particles and fibres for pharmaceuticals [36], paint and composite applications thin films for large coatings, microelectro mechanical systems/devices [37], drying materials like high porosity gels in separation science, petrochemical separations and purification [38], industrial food processing, chromatography for analysis, preparation and characterization of samples [39]. Super critical fluids are also used for controlling chemical reactions [40], waste destruction, recycling [41], and earth sciences for sample preservation [42].

Under normal drying conditions, a naturally porous or spongy structure can undergo large capillary forces that degrade the micro structure of the material resulting in degradation or severe collapse of the microstructure resulting in shrinkage. Depending on the surface tension of the liquid, the molecules in the liquid are strongly attracted and the capillary stress exerted on the pores of the material will be higher. The pressure difference between a gas and liquid phase is given by the Laplace equation [43]

\[ P_g - P_l = \frac{2\gamma}{R} \cos \theta \]
Where $P_g$ and $P_l$ are the gas pressures, $\gamma$ is the surface tension, $R$ is the radius of the tube or capillary and $\theta$ is the wetting angle. If the pore size in a material is of the order of a few nanometres and we assume complete wetting making the contact angle zero, the capillary stresses that occur are in the order of tens of mega Pascal with $\gamma$ of water 72.9 mN/m and ethanol 22.3 mN/m. These stresses cause shrinkage and cracking during drying as a result of capillary tension in the liquid since it is not uniform over the entire network [43].

In order to overcome these stresses and prevent shrinkage during processing, a process by which a liquid is initially exchanged by diffusion from a material by a liquid with low critical temperature and pressures is desirable. A list of common liquids used for SCD and water are shown in Table 2.2 [44]. After the solvent exchange, the liquid is then compressed and heated beyond its critical point. The pressure is then gradually released allowing the gas to escape leaving a dried product. This is all done without crossing the liquid-gas boundary on the phase diagram, instead going through the supercritical region where there is no distinction between liquid and gas. This is shown by the path marked $A\rightarrow B\rightarrow C\rightarrow D$ by the arrows in the pressure—temperature phase diagram shown in Error! Reference source not found..

Sensors were made by super critical drying of the gelatinous precipitate exchanged with dry ethanol and water exchanged RuO$_x$(OH)$_y$ gels. Figure 2.14a shows the gold interdigitated electrodes before the deposition of RuO$_x$(OH)$_y$, Figure 2.14b were the electrodes after RuO$_x$(OH)$_y$ deposition and Figure 2.14c is one electrode dried with the super critical dryer and the other allowed to dry in air. The resulting interaction with carbon monoxide at room temperature of two sensors made with RuO$_x$(OH)$_y$ exchanged with ethanol and water is shown in Error! Reference source not found.. The effect of film thickness and change in resistance on exposure to carbon monoxide is shown in Figure 2.16. The sensor formed from the thick film of
RuO$_x$(OH)$_y$ upon exposure to carbon monoxide shows an increase in resistance but the resistance does not stabilize within the time of this experiment while the thin RuO$_x$(OH)$_y$ sample shows a rapid rise in resistance followed by a stabilization in the resistance (indicated by no change in the resistance) within a few minutes of exposure to 1000 ppm carbon monoxide. The response times ($t_{90}$, time to reach 90% of the signal at each exposure time) for the thin and thick films are 5.8 minutes for the thin sensor and 7.3 minutes for the thick film sensor.

2.4. Discussion

The primary focus of this discussion is to examine the reactivity of CO on RuO$_x$(OH)$_y$ and correlation of the reactivity patterns with the resistance changes of RuO$_x$(OH)$_y$ upon exposure to CO. The catalytic activity of RuO$_x$(OH)$_y$ towards CO oxidation under ambient conditions has been previously examined as a function of heat treatment of RuO$_x$(OH)$_y$ [15]. It is reported that the untreated as-synthesized samples have negligible catalytic activity, the activity increases upon heating the sample, with the optimum temperature being 150-250$^\circ$C (CO conversion of 42.46%), and decreases significantly for samples heated at 450-600$^\circ$C[15]. Thus, both as-synthesized RuO$_x$(OH)$_y$ and crystalline RuO$_2$ obtained from heating the RuO$_x$(OH)$_y$ beyond 500$^\circ$C are poor ambient condition CO oxidation catalysts, yet the change in electrical properties (Figure 2.10) as reported in this work upon exposure to CO is very different. As-synthesized RuO$_x$(OH)$_y$ exhibits marked changes in resistance with CO and RuO$_x$(OH)$_y$ heated beyond 500$^\circ$C (converted to crystalline RuO$_2$) exhibiting no change at all.

2.4.1. Reactivity of CO with RuO$_x$(OH)$_y$
The changes in the infrared spectra in the 1000-1700 cm\(^{-1}\) region (Figure 2.7b) upon exposure of RuO\(_x\)(OH)\(_y\) to CO suggest formation of monodentate, bidentate and bicarbonate species as seen in Table 2.1 [31-34]. The formation of these CO\(_2\)-derived carbonate/bicarbonate species indicates that CO oxidation is taking place. Eventually with flow of air over the sample (150 min), the surface is completely regenerated (Figure 2.7a). However, treatment in air for a limited time (30 min) leads to an intermediate stage in this cycle and provides more insight into the reactivity. Bands are observed due to chemisorbed CO at 2043 and 2059 cm\(^{-1}\) (Figure 2.7c) which are characteristic of CO binding to a Ru site on RuO\(_2\) [45]. In addition, the band at 2003 cm\(^{-1}\) is typical of CO adsorption on a coordinatively unsaturated Ru site on RuO\(_2\) (oxygen vacancy) [45]. The band at 2354 cm\(^{-1}\) is due to adsorbed CO\(_2\) since P and R branches typical of the gas phase are not being observed, and show that the regeneration of the sample in air leads to CO\(_2\) formation. Exposure to flowing air also leads to the loss of the monodentate carbonate bands at 1433, 1311 and 1167 cm\(^{-1}\) (compare Figure 2.7b and 2.7c). Interaction of the RuO\(_x\)(OH)\(_y\) surface with CO also leads to changes in the OH stretching region, loss of high frequency OH groups (3618 cm\(^{-1}\)) and generation of water (3367 cm\(^{-1}\)) (Figure 2.7b). The surface of RuO\(_x\)(OH)\(_y\) is also reactive to CO\(_2\) (Figure 2.7d), and the carbonate/bicarbonate bands are similar to the partially air-treated sample after reaction with CO (Figure 2.7c).

We propose the following reactions on RuO\(_x\)(OH)\(_y\).

\[ -CO_{(ad)} + -OH + O_o \rightarrow -HCO_3{(ad)} \tag{2} \]
\[ -HCO_3{(ad)} + -OH \rightarrow -CO_3{(ad)} + H_2O_{(ad)} \tag{3} \]

The reaction with O\(_o\) (lattice oxygen) on the RuO\(_x\)(OH)\(_y\) leads to reduction in the metal. It has been noted that redox active metal oxides such as iron oxide [46] and cobalt oxide [47,47] are more active in CO oxidation. CO oxidation on iron oxide is shown to occur by abstraction of
lattice oxygen from Fe₂O₃ (Fe(III)) to form Fe₃O₄, (Fe(II,III). In the instance of cobalt oxide, CO oxidation is proposed to occur by an initial CO adsorption event on a lower oxidation state of cobalt Co(II), which interacts with a neighboring oxygen bound to a higher oxidation state cobalt Co(III), to form carbon dioxide. The oxygen lost in these reactions is then replaced by the oxygen present in the gas mixture. The overall increased activity is due to the availability of “active” oxygen and the accommodation of oxygen vacancies by redox active metal oxides [46-48]. Oxygen from the gas phase can replenish the oxygen vacancies and regenerate the sample.

Evidence for the reduction in ruthenium also comes from the CO chemisorbed band at 2003 cm⁻¹ (Figure 2.7c), which is in the frequency ~2000cm⁻¹ range assigned to CO adsorbed on oxygen vacancies [45]. Overall, CO oxidation is leading to a reduction of the RuOₓ(OH)ᵧ surface, formation of CO₂ leading to carbonate/bicarbonate formation involving the OH groups of RuOₓ(OH)ᵧ and the oxygen vacancies are being occupied by CO. The adsorbed water is formed by reaction of bicarbonate with –OH.

CO oxidation over RuO₂(110) has been studied extensively [10,49-52]. Two prominent active sites for reactive oxygen have been identified, a bridge site and oxygen on coordinatively unsaturated Ru atoms as seen in Figure 2.18. The high catalytic activity is attributed to CO adsorbed on the unsaturated site reacting with the oxygen either on the unsaturated site or with the oxygen at the bridge site [51,52]. Thus, the mechanism is still controversial, centered on which oxygen is more reactive. Comparison of the mechanism of CO oxidation on RuO₂(110) to CO oxidation on RuOₓ(OH)ᵧ is unclear, though, the kinetic data (activation energy) for CO reaction on single crystal RuO₂(110) at 10⁻⁷ mbar pressure of 56 kJ/mol [50] was comparable to CO oxidation at ambient pressure on particles derived from a low temperature thermal treatment of RuOₓ(OH)ᵧ of 36 kJ/mol [15]. There are also other parallels: on single crystal RuO₂(110)
surface, the vibrations of chemisorbed CO at the oxygen vacancy sites are observed at 1995, 2072 and 2135 cm\(^{-1}\) [45,49], we observe bands at 2003, 2043 and 2059 cm\(^{-1}\). This strongly held CO on RuO\(_x\)(OH)\(_y\) is not removed readily with O\(_2\), a similar observation is made from experiments involving reaction of CO-bound RuO\(_2\) (110) with O\(_2\) [50]. The carbonate observed upon reaction of CO\(_2\) on RuO\(_2\) (110) leads to monodentate (1216 and 1410 cm\(^{-1}\)) [53], with RuO\(_x\)(OH)\(_y\) we observe bicarbonate and bidentate carbonates (Figure 2.7d). As-synthesized RuO\(_x\)(OH)\(_y\) is known to be a poor CO oxidation catalyst [15], and we propose that the product of the oxidation CO\(_2\) is held as carbonates/bicarbonates which block active surface sites. Surface poisoning has also been noted for single crystal RuO\(_2\) (110) due to the formation of carbonate and bicarbonate species [53,54], with the latter being proposed as the major deactivating pathway [54]. Water adsorption on Ru sites in RuO\(_2\) (110) has also been proposed to act as deactivating the catalysts [55]. Carbonate poisoning is also reported on Co\(_3\)O\(_4\) [48]. Carbonate and bicarbonate bands are also formed on exposure of Fe\(_2\)O\(_3\) to CO [46], and the formation of the oxygenates involve the reaction of CO\(_2\) with -OH groups. Water production during CO oxidation on Au/Fe\(_2\)O\(_3\) has been noted [31].

There are three possible scenarios to interpret the changes in resistance observed with CO. Resistance changes due to formation of carbonate species has been noted for neodymium oxide carbonate upon exposure to CO\(_2\) and H\(_2\)O [56]. The basis for the electrical activity was the reaction between CO\(_2\) and surface-adsorbed OH groups. However, in the present study, no resistance change was observed upon exposure of RuO\(_x\)(OH)\(_y\) to CO\(_2\), though carbonate formation was observed. Thus, even though CO\(_2\) reacts with the OH groups in RuO\(_x\)(OH)\(_y\), as in the neodymium oxide carbonate, the resistance change must arise from a different pathway in RuO\(_x\)(OH)\(_y\).
The second scheme is based on the supercapacitor literature related to RuO$_x$(OH)$_y$, where electronic conductivity between the particles is proposed to occur by electron hopping across small rutile-like 20-50 nm nanocrystals in a percolative fashion, with the OH/H$_2$O adsorption layer between the particles forming the barrier through which the electron needs to move as shown in Figure 2.17 [11-13]. Thus, any interference to this hopping process will decrease conductivity. As shown in Figure 2.7, the IR spectra indicates that carbonates are adsorbed to the RuO$_x$(OH)$_y$ surface in the presence of CO. The carbonates formed on the surface of RuO$_x$(OH)$_y$ will impede the electron hopping between the RuO$_2$ crystallites in the RuO$_x$(OH)$_y$ network. However, this mechanism cannot be correct, since CO$_2$ also creates carbonates, but results in no change in resistance.

The third scheme involves the influence of the lower valent states of ruthenium on the electronic conductivity of RuO$_x$(OH)$_y$. In RuO$_x$(OH)$_y$ as supercapacitor, the electron capture results in reduction of ruthenium (Ru$^{4+}$ → Ru$^{3+}$, Ru$^{2+}$), indicating that multiple valences are readily accessible. The origin of electronic conduction in these mixed ion-conducting materials has been correlated with an electron hopping between the 3+ and 4+ oxidation states [57,58]. Hydrated RuO$_x$ in hydroxyapatite has been reported to be reduced by CO under ambient conditions to a lower valence state [59], and reduction of the RuO$_2$ layer on ruthenium catalysts during CO oxidation has also been observed [35]. Impedance spectroscopic studies on RuO$_2$-TiO$_2$ aerogels under both dry and humid conditions suggest that increase in oxygen pressure can result in enhanced electronic conductivity [60]. This increase in electronic conductivity in the presence of O$_2$ has been explained as due to oxidation of Ru$^{3+}$ to Ru$^{4+}$. Data presented in the present study shows that lower valent states of Ru are present in RuO$_x$(OH)$_y$ (XPS), and the IR studies show that CO oxidation is taking place, abstracting oxygen from RuO$_x$(OH)$_y$ and leading to reduction.
of the material. The lower valent states of Ru will lead to increased resistance which is reverted in the presence of oxygen, as the vacancies are filled and the adsorbed carbonates/bicarbonates/water is lost.

With heated samples of RuO$_x$(OH)$_y$, the conductivity changes observed under ambient conditions in the presence of CO gradually disappears. There are four changes that occur upon heating RuO$_x$(OH)$_y$ - loss of water and the hydroxyl groups (as evidenced by TGA), the lower valent states of ruthenium are transformed to Ru(IV) (XPS) and the disordered RuO$_x$ units assemble to form crystalline RuO$_2$ (XRD) and there is an increase of particle size with annealing (XRD). With heating of RuO$_x$(OH)$_y$, it is reported that the CO oxidation at ambient conditions is diminished, and the reason proposed is that the surface area of the material is decreasing [15]. It is known that bulk crystalline RuO$_2$ is a metal and thus electron compensation upon CO oxidation can readily occur. We propose that this is the primary reason why there is only a minimal change in conductivity with CO (Figure 2.1).

2.4.2. Sensor Performance

The performance of a sensor can be described by its detection limits, response times, sensitivity, long term stability and selectivity. The response of the device to CO (32 -1000 ppm) as observed in Figure 2.5 and Figure 2.11 shows stability with repeated cycling, though passing dry gases over the sample for times > 16 hours does begin to decrease the signal. This loss in signal with long testing times could be due to loss of hydroxyl groups, or due to strong adsorption of carbonate species that are not being removed by the air treatment, as evidenced in the infrared (Figure 2.7). An experiment was carried out where a sample was exposed to dry air for 16 hours and then the sensing tests were performed. The sensor performed as well as a sensor that was not
subjected to flowing gas. Thus, we propose that the sensor may be losing response at long times because of the carbonate adsorption, and inclusion of catalysts on the ruthenium oxide surface may alleviate this problem. We propose that the detected concentration can be lowered further than 32 ppm. The reproducibility of device fabrication is confirmed by the testing of multiple devices (Figure 2.11). The as-synthesized RuO$_x$(OH)$_y$ without heat treatment is the most sensitive to CO and discriminates against 150 ppm NH$_3$, 15 ppm NO,15 ppm NO$_2$,1000 ppm propane,1000 ppm methane, 2000 ppm CO$_2$, with R/R$_o$ of 1, which makes it attractive for use in CO detection in ambient conditions. The advantage of the present device is that it operates at room temperature requiring no heat and hence suitable for low power applications. Typically, metal oxide semiconductor sensors based on TiO$_2$ [16], SnO$_2$ [20] operate at high temperatures (>250$^\circ$C) since oxygen vacancies are necessary for electronic conduction. Also, semiconductor sensors usually show interference to other gases (e.g. hydrocarbons) that react on the oxide surface.

2.4.3. Performance of Supercritical Dried Ru$_x$(OH)$_y$

The device made from RuO$_x$(OH)$_y$ from water via super critical drying in Figure 2.15 shows a larger change in resistance (average R/R$_o$~1.3) than RuO$_x$(OH)$_y$, dried from ethanol (average R/R$_o$~1.1). So water is used for the final centrifugation of RuO$_x$(OH)$_y$ and dry ethanol is used at the last step as the exchange solvent. Figure 2.16 shows that as the amount of RuO$_x$(OH)$_y$ deposited on the electrodes is varied, the thickness of the resulting sensing layer also changes. The data show as the RuO$_x$(OH)$_y$ layer becomes thinner there is a faster change in resistance with a response time $t_{90} = 5.8$ min for thin film and $t_{90} = 7.2$ min, upon exposure to CO. In trying to optimize this device this supercritical drying showed promise but there were no significant
improvements in the sensitivity, response/recovery times over the original preparation method \((R/R_o = 4, t_{90} = 6 \text{ min})\). The retention of the original porosity of the films by super critical drying is still a promising method for the preparation of these devices as less material is needed for making each device. Also a finer control of the device preparation and quantification of the change in porosity would give a better indication of the promise of this method for the optimization of the \(\text{RuO}_x(\text{OH})_y\) sensor.

2.5. Conclusion

\(\text{RuO}_x(\text{OH})_y\) was synthesized by reaction of alkali with a solution of \(\text{RuCl}_3.x\text{H}_2\text{O}\). The material was amorphous with hydroxyl groups, water and mixed valent ruthenium (Ru (III) and Ru(IV)). The drying of \(\text{RuO}_x(\text{OH})_y\) by the super critical method did not have an improvement on the sensing properties of this device. The conductivity of the material decreased upon exposure to CO and recovered after passing air over the sample. Infrared spectroscopy showed the presence of carbonate and bicarbonates on the \(\text{RuO}_x(\text{OH})_y\) surface with CO. Upon heating the \(\text{RuO}_x(\text{OH})_y\), the crystalline form of \(\text{RuO}_2\) was obtained, but this material showed no change in resistance with CO. A mechanism involving the redox state change in \(\text{RuO}_x(\text{OH})_y\) upon reaction with CO is proposed for explaining the conductivity changes. The change in conductivity of \(\text{RuO}_x(\text{OH})_y\) is suitable for the detection of carbon monoxide at room temperature. The sensing tests show that the selectivity and detection limits have the potential to make this device a practical CO detector for low power applications.
References


### Table 2.1 Vibrational frequencies of carbonyl, carbonate and bicarbonate species

<table>
<thead>
<tr>
<th>Species</th>
<th>Molecular Structure</th>
<th>Vibrational Frequencies $v$(cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Gas phase CO</td>
<td>$\ce{C=O}$</td>
<td>2150</td>
<td>[32,34]</td>
</tr>
<tr>
<td>Monodentate CO</td>
<td>$\ce{M-C=O}$</td>
<td>2003 2043 2059</td>
<td>[32,45,49]</td>
</tr>
<tr>
<td>Adsorbed CO$\text{}_2$</td>
<td>$\ce{M-CO}_2$</td>
<td>2354 2333</td>
<td>[47]</td>
</tr>
<tr>
<td>Monodentate carbonates</td>
<td>$\ce{M=O--C=O^-}$</td>
<td>1433 1311 1167</td>
<td>[32,34,61]</td>
</tr>
<tr>
<td>Bidentate carbonates</td>
<td>$\ce{M=O--C=O}$</td>
<td>1539 1281 1515 1297</td>
<td>[32,34]</td>
</tr>
<tr>
<td>Bicarbonates</td>
<td>$\ce{M=O--C=O}$</td>
<td>1617 1038 1050 1620</td>
<td>[31,32,61]</td>
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<tr>
<td>Water</td>
<td>-OH</td>
<td>3367 3618 3426 3410</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>Bending mode 1650</td>
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Table 2.2 Critical temperature ($T_c$) and pressure ($P_c$) of fluids

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$ (°C)</th>
<th>$P_c$ (Psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>241</td>
<td>890.097</td>
</tr>
<tr>
<td>Methanol</td>
<td>238.5</td>
<td>1172.485</td>
</tr>
<tr>
<td>Acetone</td>
<td>235.1</td>
<td>681.677</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>235.3</td>
<td>690.960</td>
</tr>
<tr>
<td>Xenon</td>
<td>16.77</td>
<td>847.165</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>31.13</td>
<td>1069.653</td>
</tr>
<tr>
<td>Hexane</td>
<td>234.6</td>
<td>438.739</td>
</tr>
<tr>
<td>Toluene</td>
<td>318.8</td>
<td>596.105</td>
</tr>
<tr>
<td>Water</td>
<td>373</td>
<td>3200</td>
</tr>
</tbody>
</table>
Figure 2.1.(a) Drop coating of a suspension of RuO$_x$(OH)$_y$ on to an interdigitated gold electrode in the fabrication of a carbon monoxide gas sensor, (b) electrode before and after coating (c) interdigitated gold electrode dimensions.
Figure 2.2. Schematic of experimental gas sensor testing apparatus
Figure 2.3. (a) Thermogravimetric analysis of RuO$_x$(OH)$_y$ (ramp rate of 10$^\circ$C/min in a nitrogen gas flow of 75cc/min) (b) XRD pattern of RuO$_x$(OH)$_y$, (c) TEM image of RuO$_x$(OH)$_y$. 
Figure 2.4 XPS spectra of RuO$_3$(OH)$_y$, (a) O 1s region: △ Ru-O-Ru, ▲ Ru-OH and ▣ Ru-H$_2$O, Ru-carbonate (b) Ru 3d region △ Ru(III) ▲ Ru(IV) and ▣ carbon 1s carbonaceous impurities and carbonates.
Figure 2.5 Changes in resistance of RuO$_x$(OH)$_y$ with repeated exposure of to 250 ppm CO in 21% Oxygen at 25°C.
Figure 2.6. Diffuse reflectance infrared spectra of RuO$_x$(OH)$_y$, (a) initial spectra, (b) spectra after first exposure to O$_2$ (21%) for 150 min, (c), spectra after CO (2000 ppm in air) exposure for 15 min, (d) spectra closed off for 45min after O$_2$ for 30min (e) Second exposure to O$_2$ (21%) for 150min (f) Exposure of (b) to CO$_2$ (25°C)
Figure 2.7 Diffuse reflectance infrared difference spectra of RuO$_x$(OH)$_y$ between (a) two O$_2$ (21%) exposures (prior and after CO exposure) (b) O$_2$ (21%) and CO (2000ppm in air) exposure (c) O$_2$ (21%) and 45min after 30min O$_2$ exposure to (b) (d) O$_2$ and CO$_2$ exposure
Figure 2.8. XRD pattern of samples obtained by heating RuO$_x$(OH)$_y$ to different temperatures (data recorded at 25°C).
Figure 2.9. (a) Ru 3d XPS spectrum of RuO₄(OH)₂ heated at 25-600°C, (b) O 1s XPS spectra of RuO₃(OH)ₓ heated at 25-600°C, (c) Ru 3d XPS spectra of RuO₃(OH)ₓ heated to 600°C: Δ Ru screened final state ▲ Ru unscreened final state for Ru(IV), (d) O 1s XPS spectra of RuO₄(OH)ᵧ heated to 600°C: Δ Ru-O-Ru ▲ Ru-OH and ▶ Ru-H₂O
Figure 2.10. (a) Change in resistance of samples obtained by heating RuO$_x$(OH)$_y$ (25-600$^\circ$C) upon exposure to 500, 250 and 1000ppm CO at 25$^\circ$C. (b) Normalized resistance change of samples obtained by heating RuO$_x$(OH)$_y$ (25-600$^\circ$C) upon exposure to 250, 500 and 1000 ppm CO at 25$^\circ$C ($R$ is resistance in CO and $R_o$ is resistance in background gas 21% Oxygen)
Figure 2.11. Change in resistance of three different samples of RuO$_x$(OH)$_y$ upon exposure to 1000, 500, 250 and 1000 ppm CO at 25°C in 21% oxygen. Inset: Normalized change in resistance on exposure to 32 ppm CO at 25°C in 21% oxygen.
Figure 2.12. Normalized change in resistance of RuO$_x$(OH)$_y$ on exposure to 250ppm CO, 2000ppm CO$_2$, 1000ppm Methane and Propane, 150ppm Ammonia, 15ppm NO and 15 ppm NO$_2$ at 25°C.
Figure 2.13. Pressure – Temperature phase diagram for carbon dioxide (CO$_2$)
Figure 2.14. (a) Gold interdigitated electrodes before deposition of RuO$_x$(OH)$_y$, (b) Electrodes after deposition of equal amounts of RuO$_x$(OH)$_y$ and (c) Electrode super critically dried on the left and electrode air dried on the right.
Figure 2.15. The effect of exchange solvent on super critically dried RuO$_x$(OH)$_y$
Figure 2.16. The effect of film thickness on response and recovery times on super critically dried RuO$_x$(OH)$_y$
Figure 2.17. Percolative fashion of electron transport in hydrated ruthenium oxide from reference [13]
Figure 2.18. Schematic from reference [39] depicting the various coordination of ruthenium present on the surface of ruthenium oxide. Coordinatively unsaturated ruthenium (Ru-cus) and bridging ruthenium (Ru-bridge)
3.1. Introduction

The reason for developing NO\textsubscript{x} sensing technologies primarily stems from three major applications, environmental, process control and biomedical. Oxides of nitrogen are important compound that exists in the atmosphere predominantly as nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) . These oxides are formed primarily via conversion of atmospheric nitrogen to nitrogen oxides occurring by very different processes, including bacterial transformations, in thunder storms, burning of biomass and engine exhausts.

In the human physiology NO is an important cell signaling molecule, acting as a vasodilator which regulates blood flow in arterioles, blood vessels in the kidneys and penis. NO also controls smooth muscle function such as the peristaltic motion of the esophagus and inhibits uterine contractions. Thus, NO is an important molecule which plays important roles in physiological and pathological functions for humans. Measurement of exhaled NO (eNO) provides a noninvasive view into the activities and diseases in the lower airways, including inflammatory response in asthma, chronic obstructive pulmonary disease and cystic fibrosis. In medical applications, breath analyzers for NO require sensitivity in the range of several ppb to 1 ppm [1,2] and selectivity to interferences to such as humidity, NO\textsubscript{2}, carbon dioxide, and carbon monoxide and hydrocarbons need to be minimized.
Various technologies have been developed for the detection of eNO and NO detection in medical settings. Chemiluminescence analyzers are most routinely used for the detection of low concentrations of NO. Although this is a reliable technique, interference from humidity, carbon dioxide, ammonia from breath samples are common, thus creating inconsistent results at different measurements from clinic to clinic and from patient to patient.

Air quality and pollution problems occur in most developed and industrial cities and is a problem of modern industrialization. The primary source of NO in the atmosphere occurs from combustion facilities and automobiles. If NO levels are left unregulated, they can cause respiratory disease, acid rain and photochemical smog. Photochemical smog is the result of a chemical reaction of sunlight with nitrogen oxides and volatile organic compounds producing particulates and ground level ozone. Environmental NOx emissions consist primarily of NO 90-95% and NO₂ and N₂O (1-4000 ppm) [3,4]. These pollution issues have fueled the development of novel detection methods for controlling and management of the pollutants. Methods for the monitoring air pollution and management include classical analytical techniques such as Fourier transform infrared spectroscopy (FTIR), gas chromatography coupled mass spectrometry (GC-MS), which are known to be selective and sensitive but are expensive, typically done offline, cumbersome and are limited by the detection limits and the response times of the instrumentation.

Another driving force for the development of NO sensors has been in the automotive industry. In the innovation and development of new internal combustion engines, the development of lean burn engines and direct-injection diesel engines to improve fuel efficiencies result in an increase in NOx emissions, with 95% of exhausts from diesel engines due largely to NO. These engines cannot employ three way catalysts for the removal of NOx from the emission streams. Thus, new
technologies for NO abatement are required. Towards this goal, a minaturizable, selective long term sensor for NO detection is required in the engine or close to the engine during operation. This would maximize the efficiency and minimize the NOx emissions of the lean burn engines.

3.2. Current Sensors for NOx Detection

Chemical sensors exist for NOx detection based on electrochemical processes such as potentiometric, amperometric and conductometric principles. Examples of a total NOx sensors are potentiometric [5] sensors based on WO$_3$/YSZ/Pt, and a similar amperometric sensor with Pt-loaded zeolite Y [6] and resistive sensors based on WO$_3$ thick films modified with noble metals [4]. These devices operate at elevated temperatures since the electronic conductivity of the semiconducting material and the electrolyte requires high temperatures for operation. Lowering the detection temperatures without compromising the selectivity would be advantageous and is the goal of the present study.

3.2.1. Lessons Learned from Hydrated Ruthenium Oxide (RuO$_x$(OH)$_y$)

The RuO$_x$(OH)$_y$ developed for carbon monoxide sensing as discussed in the previous chapter will form the premise for the discovery of other novel materials for nitric oxide (NO) gas sensing applications. Hydrated RuO$_2$ was shown to be a selective sensor for carbon monoxide under ambient conditions, and the sensing mechanism is dependent on three factors:

- A metal oxide with a mixed oxidation state, ruthenium being present as Ru(III) and Ru(IV)
- Degree of hydration (20-50%) and presence of hydroxyl groups
- Selectivity to carbon monoxide oxidation at ambient conditions
In the continuance of this novel discovery and to capitalize on this idea a closer look was made at other conducting metal oxide materials. Table 3.1 Conductive metal oxide candidates for low temperature gas sensing and their properties summarizes the materials, the conductivity and the crystal structure of the room temperature polymorph of a variety of conducting metal oxides. RuO$_2$, VO$_2$, WO$_2$, ReO$_2$, IrO$_2$, OsO$_2$, NbO$_2$, MoO$_2$, TcO$_2$, RhO$_2$, PtO$_2$. The purpose of this work was to develop a low temperature sensor for the detection NO. A material with similar properties as those found pertinent in the carbon monoxide sensor is present in vanadium oxide, and are as follows:

- A material with appreciable room temperature conductivity
- A catalyst for NOx reduction
- A candidate with multiple stable oxidation states at room temperature

### 3.3. Properties of Vanadium Oxides

Vanadium oxides have been studied over the years for various applications. The principal oxides of vanadium occur in oxidation states from V$^{2+}$ - V$^{5+}$, and the known oxides are, vanadium monoxide (VO), vanadium dioxide VO$_2$, vanadium trioxide (V$_2$O$_3$) and vanadium pentoxide (V$_2$O$_5$). There also exists mixed valence complexes of vanadium oxides Wadsley phase V$_{2n}$O$_{2n-1}$ (V$_6$O$_{13}$, V$_4$O$_7$), and Magnéli phase V$_{n}$O$_{2n-1}$ (V$_3$O$_5$) [7].

Vanadium pentoxide in its pure form is considered to be an insulator. The non-stoichiometric polymorph of V$_2$O$_5$ exhibits electrical conductivity due to the presence of oxygen vacancies [8]. The number of oxygen vacancies and their density depend on the synthetic route employed in the fabrication of V$_2$O$_5$ crystals. The presence of V$^{4+}$ in the V$_2$O$_5$ is related to the oxygen vacancies and the conductivity [9] (V$^{4+}$ $\rightarrow$ V$^{5+}$+e$^-$), thus making the charge carrier density directly
proportional to the density of oxygen vacancies. The non-stoichiometric oxide created by the absence of oxygen atoms (oxygen vacancies) and vanadium as $V^{4+}$ results in mobile electrons, the dominant charge carrier of $V_2O_5$ and determines the conductivity of the material.

3.3.1. Interaction of NO with Vanadium pentoxide

Vanadium pentoxide has been used as a catalyst for the selective catalytic reduction (SCR) of NO$_x$ by ammonia, for the removal of NO$_x$ from stationary sources such as power plant flue gases since the 1980’s [10]. NO is also a large part of diesel engine exhausts (95%). SCR catalysts typically reduce NO to N$_2$ at 250-450° C. The following reaction has been proposed to occur on the vanadium oxide during the reaction.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$  \hspace{1cm} (1)

Although the mechanism for this reaction has not been completely proven, it is suggested that the catalytic efficiency is dependent on a combination of factors [11]

- Surface morphology and structure
- Strength and number of V=O bonds
- Acidity of the surface vanadium oxide
- Ease of reduction of vanadium catalyst

Some of these factors that are important in the catalytic reduction process may also be relevant in understanding the basis of the resistance changes observed for $V_2O_5$ upon interaction with NO as a function of concentration, temperature and preconditioning. Catalytic studies [12] on the effect of the crystal morphology on selective catalytic reduction (SCR) of nitric oxide over $V_2O_5$ have shown differences in conversion rates and yields of reduced products. These differences are
attributed to the amount of V=O sites present on the crystal surface as compared with V-O-V sites, each site promoting competing reactions.

3.4. Gas Sensing Applications of Vanadium Oxides

Vanadium oxides have been used for various gas sensing applications, the oxides have been used as thin films, nanoparticles, nanotubes/fibers, and vanadium doped into metal oxides. Representative examples are discussed below.

3.4.1. Sulfur Dioxide (SO$_2$)

A gas sensor [13] selective to sulfur dioxide (SO$_2$) in the presence of other gases like carbon monoxide, methane and butane was developed based on vanadium doped tin dioxide. This resistive based sensor operates at 350°C and detects 5 ppm SO$_2$, which is the OSHA upper limit for short term exposure over an 8 hr period with slight interferences from reducing gases such as 100 ppm carbon monoxide, methane and butane.

3.4.2. Hydrocarbons

Vanadium oxide supported on aluminum oxide (Al$_2$O$_3$), titanium oxide (anatase TiO$_2$), zinc oxide (ZnO) and zirconium oxide (ZrO$_2$) [14], has been used in the detection of liquefied petroleum gas (LPG). The sensor detects 400 ppm liquefied petroleum gas (LPG) which is lower than the flammability limit of 1000 ppm in air at 300°C and is unaffected by humidity. The sensing is proposed to occur by surface reduction of V$_2$O$_5$ to VO$_2$. Benzene is another analyte that has been detected by a vanadium and tantalum-doped titanium oxide (TiTaV) [15]. The sensor optimally works at 380°C and detects concentrations as low as 10 ppm with minimal interference from carbon monoxide even at concentrations an order of magnitude higher than
benzene. The improvement of this composite, vanadium and tantalum-doped titanium oxide sensor is proposed to be from the merging of the positive effect of tantalum, which reduces grain growth in titania and the catalytic properties.

3.4.3. Humidity and Ethanol

Humidity sensing [16] has been explored by vanadium complexes such as hydrated poly vanadium-molybdenum acid. The resulting gels have a composition of \( \text{H}_2\text{V}_{12}\text{O}_{30,7-8.4}\text{H}_2\text{O}, \text{H}_2\text{V}_{11}\text{MoO}_{31,2-8.4}\text{H}_2\text{O}, \text{H}_2\text{V}_{10}\text{Mo}_2\text{O}_{31,7-8.6}\text{H}_2\text{O} \) and \( \text{H}_2\text{V}_9\text{Mo}_3\text{O}_{32,3-9.0}\text{H}_2\text{O} \). Gels were made by hydrothermal methods and screen printed on to substrates. A pellet is then made with the substrate sandwiched or coplanar with nickel electrodes, the conductivity and the capacitance of the device is measured by ac impedance spectroscopy as the humidity was varied from 20-97%.

Hydrothermally synthesized vanadium oxide nanobelts [17] have been developed for ethanol sensing. These devices are operational at temperatures as low as 150°C and do not show large drifts with changing relative humidity. Nanobelts of vanadium oxide have also been coated with tin, titanium and iron oxide nano particles [18] to improve the sensitivity of these nanobelts to ethanol and showed good response within 5-250 ppm. The improved sensitivity is due to the change in the electronic transport mechanism on the surface of the nanobelts due to the metal oxide coating. The mixed vanadium tin, titanium or iron oxide coating on the nanobelts improved the gas sensing by modifying the electron transport, with the metal oxide grain boundaries dominating the device response to different gases. The coated nanobelts in addition to ethanol show sensitivity to gasoline, and hydrogen sulfide at 100 ppm at 200°C. Thin films of rf sputtered vanadium oxide [19] have also been used for ethanol detection in the range 200-1400 ppm at 300°C in air. This study shows the film sputtered in 15% oxygen in argon gives the best sensitivity to ethanol with minimal interferences from other gases such as carbon dioxide, carbon
monoxide and methane. Iron oxide activated vanadium oxide nanotubes [20] have also been used for ethanol sensing at 230°C-330°C at 30-40% relative humidity in air. This device has good range of detection from 10-1000 ppm. The iron oxide nanoparticles on the surface of the vanadium oxide increase the number of active sites for the adsorption of analyte gas molecules. This increased number of active sites makes the device better than vanadium oxide alone making it a good sensor selective to ethanol over toluene.

3.4.4. Carbon Monoxide

Carbon monoxide (CO) has also been detected by iron doped vanadium-tin oxide (FeVSn) nanocrystallites [21]. The resistive sensor detects 50-500 ppm CO at an optimal temperature of 200°C with an operational temperature range of 150-225°C. The doping with iron is reported as the reason for the lowering of the operating temperature and faster response times as compared to an undoped vanadium-tin oxide (VSn) complex. Alkali-metal cations such as M = Na, K Rb, Cs (sodium, potassium, rubidium and cesium) [22] when doped in vanadium oxide results in formation of M_xV_2O_5 which has been reported to be sensitive to hydrogen, carbon monoxide and ammonia. Impedance spectrometry was used to measure the resistances of the device and optimal gas sensing was observed at 80-100°C with response times of 2-3 min and good sensitivity to hydrogen, carbon monoxide, and ammonia in concentration ranges from 0.1-80, 0.1-5 and 0.1-5%.

3.4.5. Amines and Ammonia

The sensing of amines and ammonia have been explored by vanadium oxides. Vanadium nanofiber chemiresistors [23] are sensitive to 9.5 ppm with a limit of detection of 30 ppb for 1-butylamine. This device is functional at 0-60% relative humidity. Aluminum (Al) and cerium (Ce) doped vanadium oxide [24] is also sensitive to 100-500 ppm ammonia at 500°C in 10%
oxygen atmosphere. This device is stable in the presence of water vapor but an increase in the response and recovery times are observed with the changes in conductivity of the sensor due to reduction of the V$^{5+}$ to V$^{4+}$ by adsorbed NH$_3$. A gasochromatic vanadium pentoxide sensor [25] for ammonia undergoes bleaching when exposed to 100 ppm aliquots due to the formation of ammonium metavanadate. This is reversed by heating of the film at 350°C. Sensors for triethylamine (TEA) have been developed using vanadium nanorods [26] and nanotubes [27]. The nanorods consist primarily of H$_x$V$_2$O$_5$·nH$_2$O and the optimum sensing for TEA occurred at 125-175°C for 10 ppm and 200°C for 0.6 ppm.

3.4.6. Nitric Oxide and Nitrogen Dioxide

Multi walled vanadium oxide nanotubes [28] at room temperature have been shown to sense high concentrations of NO, NH$_3$ and O$_2$ (25-100%). Changes in permittivity and conductivity of the nanotube layers are monitored as a function of concentration and analyte gas. NO concentrations were also measured in the range 50-650 ppm by vanadium oxide [29], with the optimum working temperature being 290°C in 10% oxygen. NO and NO$_2$ have been both detected by vanadium composites [30] of aluminum oxide (V$_2$O$_5$·Al$_2$O$_3$) and zinc oxide (V$_2$O$_5$·ZnO). The p-n junctions formed by the p-type and n-type semiconductor composites provide opportunity for gas sensing applications. Optimal sensing occurs at 400°C for both NO and NO$_2$ within the tested concentration range of 20-300 ppm with a lower sensitivity to NO$_2$. A mixture of vanadium and aluminum oxide [31] shows better sensitivity to NO and NO$_2$ than each of the individual oxides. The increase in adsorption sites by mixing the two oxides is suggested as the reason for the composites increased effectiveness. Chemically vapor deposited vanadium oxide [32] is sensitive to 10-90 ppm NO$_2$, with the sensitivity depending on the precursor and deposition temperature. The optimum sensing film was deposited from vanadium oxytripropoxide (VO(OC$_3$H$_7$)$_3$) at
350°C. Vanadium and tungsten oxide layered composites [33] have also shown sensitivity to NO₂ at 250°C, with the composite out performing each of the individual oxides. Concentrations as low as 2-10 ppm were studied with a change in resistance three times the original (800KΩ → 2400KΩ for 6 ppm) and a complete recovery of the baseline when exposed to air. Higher concentrations of NO₂ have been sensed on sputtered vanadium oxide [34] thin films in a 15% oxygen atmosphere. The optimum working temperature is 280°C to 100-500 ppm NO₂ and the increased sensitivity is attributed to the open grain structure and increased porosity of the film. Vanadium modified MCM-41 [35] thin films have been used as gas sensors for NO₂ operable at room temperature. This device is made of a thin film of vanadium modified mesoporous silica used as the insulator layer applied on a metal insulator semiconductor structure (MIS). This structure is used as a surface photo voltage (SPV) sensor. The resulting sensor is sensitive to NO₂ down to 350 ppb in nitrogen and up to 1.5 ppm. The sensor consist of vanadium modified mesoporous MCM-41 thin films deposited on a 100 nm Si₃N₄ layer on a 100 nm SiO₂ substrate layer and sandwiched between a metal (gold) and semiconductor layer (n-Si). Sensing is attributed to changes in the charge on the semiconductor surface and a change in the dielectric constant upon the adsorption of gas molecules.

Radio frequency (rf) reactive sputtering was used to make vanadium oxide films [36] with varying oxygen atmospheric concentrations. A film prepared in 15% oxygen shows the best sensitivity to 100-900 ppm NO₂ at 280-300°C. The film also shows sensitivity to ethanol, and smaller but notable sensitivity to carbon monoxide, methane and carbon dioxide (>500 ppm). Vanadium oxides and vanadium doped materials have been used for the detection of sulfur dioxide, carbon monoxide, water, ethanol, benzene, liquefied petroleum gas, ammonia, amines nitric oxide and nitrogen oxides. These examples use vanadium oxide as a resistance based
device. The sensing mechanisms involved the interaction of the analyte gas and the variable oxidation states of the vanadium oxide ($V^{2+} \rightarrow V^{5+}$) or one of the dopants in the individual device. These sensors are often not very selective to analyte gases. Also in some of the sensors, the vanadium doping served to lower the operating temperatures of the devices.

The goal in this work is to understand the resistance changes of vanadium oxides with exposure to NO and also the potential of these materials for ambient condition sensing of NO.

### 3.5. Experimental Section

3.5.1. Materials Synthesis

3.5.1.1. Vanadium pentoxide ($V_2O_5$)

Vanadium pentoxide used in all the experiments was obtained from Alfa Aesar (99.9 % metals basis). The as obtained materials were examined and as well as materials heated at 100°C- 600°C for 4 hours in flowing air.

3.5.1.2. Vanadium dioxide ($VO_2$)

Nanocrystalline vanadium dioxide was synthesized by previously established methods [37]. A 1.81g of Vanadium oxide ($V_2O_5$) was dispersed in 30 ml of 37% formaldehyde by stirring for 2 hr. This resulted in the formation of a yellow suspension. The resulting suspension was placed in two Paar bombs and hydrothermally treated for 2 days at 180°C. After 2 days the bombs were cooled to room temperature, the resulting blue-black meta-stable powder was washed with two 10 mL aliquots of water, ethanol and diethyl ether and dried overnight at 70°C in a vacuum oven. A final heat treatment was done by heating the meta-stable sample in argon at 700 °C for 1 hr.
3.5.2. Materials Characterization

3.5.2.1. Scanning Electron Microscopy

A Quanta 200 with a tungsten oxide filament is used for the electron microscopy of the samples after they are coated with a thin layer of gold by sputtering.

3.5.2.2. X-Ray Diffraction

A Rigaku Geigerflex X-ray diffractometer with Ni-filtered Cu Kα radiation was used for powder diffraction measurements.

3.5.2.3. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

This was carried out in a controlled environment cell (Pike Technologies) with a ZnSe window in a Perkin Elmer Spec400 spectrometer. Certified mixtures of NO, 1000 ppm in N₂ (Praxair) and 21% oxygen in nitrogen (Praxair) were used with gas flow rates of 60 cc/min. Scans were collected in the range 4000-850 cm⁻¹ with a resolution of 4 cm⁻¹. All spectral subtractions were done with the Spectrum 6.3.1 software (Perkin Elmer). A mercury cadmium telluride (MCT) detector was used for the IR measurements.

3.5.2.4. X-ray Photoelectron Spectroscopy

The Kratos AXIS Ultra X-ray photoelectron spectrometer (XPS) with an Al source was used for all XPS analysis. A 13 kV voltage with a 10 mA current and pass energy of 20 eV at 0.1 eV resolution was used. CasaXPS Version 2.3.15 software was used for the deconvolution of the XPS data. A Shirley background was used for all data processing. The binding energies were calibrated relative to the C 1s peak at 285 eV.

3.5.2.5. Resistance Measurements

Alumina substrates (10 mm x 10 mm) with interdigitated gold lines of 0.25 mm spacing were obtained from Case Western Reserve University Electronics Design Center. Gold lead wires
(Alfa Aesar, 99.99%) were connected with gold paste (Heraeus). The electrodes were heat treated at 600°C for 3 hours in order to remove organic binders from the gold paste. The V₂O₅ and VO₂ particles were suspended in water (5% by weight) by sonication. The suspension was drop coated onto the electrodes and allowed to dry in air for 4-6 hrs.

All tests were done within a quartz tube housed in a temperature programmable furnace (Lindberg Blue, TF55035A). Measurement protocol consisted of flowing various volumes of certified mixtures of nitrogen oxide 30 ppm and 1000 ppm, nitrogen dioxide 1000 ppm in N₂ (Praxair), 50% oxygen in N₂ (Praxair) and nitrogen (Praxair) over the devices to give 15-1000 ppm in 21% oxygen (air), balanced with nitrogen in order to keep the flow rate constant. Certified premixed carbon monoxide 2000 ppm in nitrogen (Praxair), propane 2000 ppm in nitrogen (Praxair), 5 ppm acetone in nitrogen and ammonia 300 ppm in nitrogen (Praxair) were used for the sensor viability studies. Gas concentrations were varied by varying the flow of each gas with Sierra Mass Flow controllers controlled by a National instruments card (NI-6703) and operated by a Labview program. Resistance measurements were made with a HP34970A at a scan rate of 0.1Hz. Tests were carried out at 25°C with a gas flow rate of 100 cc/min for all experiments.

3.6. Results

3.6.1. Materials

The vanadium pentoxide obtained from Alfa Aesar was examined by SEM and the particles are observed to be a distribution of irregular shaped 100-500 nm particles as shown in Figure 3.1. The synthesized vanadium dioxide has a different morphology from the vanadium pentoxide as shown in Figure 3.4. The particles are uniform rods and are observed to have a size of 1 x 5µm.
3.6.2. Characterization of V$_2$O$_5$

Figure 3.2 shows the X-ray powder diffraction of the as obtained vanadium pentoxide particles and indicates that the particles are crystalline. The dominant peaks near 20° and 30° (2θ) correspond to the (001) and (110) reflections of the orthorhombic V$_2$O$_5$ structure.

X-ray Photoelectron Spectroscopy of V$_2$O$_5$ in the V 2p and O 1s region is shown in Figure 3.3. Three bands are observed, two arise from the V2p $^{3/2}$ and $^{1/2}$ electrons at 517eV and 524eV respectively, and one is due to oxygen 1s at 530eV [38]. The peak at 517eV is further deconvoluted into two components, indicating multiple vanadium species are present in the material. The smaller peak V2p $^{3/2}$ at 515.8eV can be assigned to V(IV) and the larger second peak at 517eV due to V(V).

3.6.3. Characterization of VO$_2$

Figure 3.5 shows the X-ray powder diffraction of the vanadium dioxide particles and indicate that the particles are crystalline and predominantly rutile VO$_2$ formed from monoclinic VO$_2$(B) [37]. X-ray Photoelectron Spectroscopy of VO$_2$ in the V 2p and O 1s region is shown in Figure 3.6. There are three bands observed, two from V2p $^{3/2}$ and $^{1/2}$ electrons at 517 eV and 524 eV respectively and one is due to oxygen 1s at 530 eV. The peak at 517 eV shows the presence of a large shoulder at 515.5 eV which is assigned to V(IV) and the second component at 517 eV is due to V(V).
3.6.4. Resistance Change with NO

The results will be presented on three samples. The first sample is made of V$_2$O$_5$ which is used as obtained, the second sample is V$_2$O$_5$ heated to different temperatures and the third sample is VO$_2$. Each of the materials is dispersed in water and deposited onto an interdigitated gold electrode to form a uniform thin film. The V$_2$O$_5$ before heat treatment is observed to be a bright yellow film while the VO$_2$ is a navy blueish film.

3.6.4.1. *Vanadium pentoxide Sample Ambient Conditions*

Figure 3.7 shows the change in resistance of the V$_2$O$_5$ sample to 15 ppm NO in an air background. There is initially a slight decrease in the background resistance with air. Upon introduction of 15 ppm NO at point (A), there is an increase in the resistance until point (B). Upon turning off the 15 ppm NO at point (C), the resistance decreases again. The cycle of air on/off and 15 ppm NO on/off is repeated a total of three times until point (E). After the fourth exposure to air (E), the concentration of the analyte gas is then changed to 500 ppm NO. An initial increase from the baseline resistance is observed in the change from point (E) to (F). Then there is a slight decrease in the resistance as shown in point (F) to (G), which then increases slightly until the 500 ppm NO is turned off at point (H). Once the 500 ppm NO is switched off (H), and the V$_2$O$_5$ sample is exposed to air, the resistance continues to increase and stabilizes until point (I). The sample is then exposed to another cycle of 500 ppm NO and the resistance decreases rapidly to point (J) and stabilizes to point (K), then it is exposed to air and the resistance increases again and stabilizes. This is repeated one more time to make a total of three cycles with 500 ppm NO.
Figure 3.8 shows the reverse of the previous experiment in that the vanadium pentoxide is initially exposed to 500 ppm NO and then exposed to 15 ppm NO. Upon the initial exposure of V2O5 sample to air the baseline gives a stable signal. Once the sample is exposed to 500 ppm NO at point (A), there is an initial increase observed in the resistance which is followed by a slight decrease at point (B) which looks like the signal is trying to reach a steady state but continues to increase at a different slope than the initial rise from the initial exposure to point (C) at which point air is introduced and NO turned off. Upon the exposure of the sample to air, the resistance increases rapidly and stabilizes at point (D), this is followed by exposure to 500 ppm NO at point (D) which causes the resistance to drop producing an initial spike at point (E) and then the resistance remains stable up to point (F). The third exposure to air and 500 ppm NO produce similar results except the increase in resistance upon exposure to air is higher (point (G) and (I)) but the decrease with 500 ppm NO is similar (point (F) and (H)). Upon exposure of the sample to 15 ppm NO at point (I), shows a different pattern, in change in resistance. Initially the resistance drops and continues to drop without stabilizing from point (I) to point (J) where the NO is turned off. Once the V2O5 sample is re-exposed to air the signal increases slightly to point (K) and proceeds to decrease to point (L). The next exposure to 15 ppm NO at point (L) shows a slight increase and stabilization of the resistance which is followed by a decrease upon exposure to air at point (M). The third exposure to 15 ppm NO at point (N) causes the resistance to increase and stabilize, and upon introduction of air at point (O), a decrease is the resistance is observed.

In summary, Figure 3.7 and Figure 3.8 show that at room temperature and ambient conditions, exposure of vanadium oxide to low concentrations of NO (15 ppm) exhibit, an increase in resistance as shown in Figure 3.7 point (A) to (B) and Figure 3.8, point (N) to (O). When the vanadium pentoxide sample is exposed to high (500 ppm) concentrations of NO there is a
decrease in the resistance of the vanadium oxide as shown in Figure 3.7 point (I) to (J) and in Figure 3.8 point (D) to (E). There appear to be transitional changes in resistance between low and high NO exposure that are unusual.

3.6.4.2. *Heat Treated Vanadium oxide*

This sample is heated for four hours in air sequentially up to 450°C, after each heat treatment, the sample is exposed to either low, (15 ppm NO) or high (500 ppm NO) in air. Initial experiments for the two concentrations were done at 25°C. Experiments of exposure to the low 15 ppm NO were done at, 150 °C, 250 °C, 350 °C and 450°C. Experiments of exposure to the high 500 ppm NO were done at 100 °C, 200°C, 300 °C and 400°C. Each of these experiments consists of two exposures of the sample to NO gas and three exposures to air. The results are shown in Figure 3.9 and Figure 3.10 for the two extreme temperatures. The ratio R/R₀ was calculated from all the temperatures and plotted in Figure 3.11, (R is the resistance of the sample after exposure to the analyte gas NO and R₀, the resistance before the gas is exposed to the analyte gas or the baseline resistance).

The initial experiment at 25°C shown in Figure 3.9 with the low 15 ppm NO shows an increase in resistance indicated by a change from point (A) to (B) and in Figure 3.11 and R/R₀ > 1. This continues to be the trend until 350°C at which point there is no significant change in the resistance of the sample when exposed to 15 ppm NO. As the temperature is increased the resistance decreases upon exposure to 15 ppm NO ( (C) to (D)) and this is depicted as R/R₀ < 1 in Figure 3.11 indicating there is a decrease in the resistance upon exposure of the sample to 15 ppm NO.
When the sample is exposed to high NO concentration (500 ppm) at 25°C in air, the resistance decreases as shown in Figure 3.10, which gives a $R/R_o < 1$ indicating there is a decrease in the resistance. The $R/R_o$ continues to decrease at higher temperatures, as shown in Figure 3.11. This trend holds within the temperatures tested (up to 400°C).

3.6.4.3.  

*NO Interaction with Vanadium dioxide (VO₂)*

Resistance measurements were done with freshly prepared VO₂ shown in Figure 3.4. The sample was made into a thin film via a water suspension. The sample is heat treated at 100 °C, 200 °C, 300 °C and 400°C for four hours exposed to 15 ppm NO and 500 ppm NO as shown in Figure 3.12 and Figure 3.13. The initial experiment at 25°C was conducted and it is observed that there are no changes in the resistance with the 15 ppm NO concentration but when the sample was exposed to the high 500 ppm NO there is an increase in the resistance of the sample. These results for the 100°C experiment show a slight increase in the baseline resistance upon exposure to 15ppm NO which becomes more prominent at 200°C and 300°C. At 300°C, the VO₂ sample shows an increase in resistance upon exposure to 15 ppm NO and an increase in resistance to 500 ppm NO. At 400°C where the device is weakly responsive to low 15 ppm NO and shows a greater increase in resistance to high 500 ppm NO.

3.6.4.4.  

*High Temperature NO and CO interaction*

The resistance changes of the vanadium pentoxide (V₂O₅) sample at 400°C is shown in Figure 3.14. The resistance of the sample is shown to decrease at low (15 ppm) and high (500 ppm) NO concentrations. The sample is exposed to 1000 ppm CO after 500 ppm NO at 25°C and 400°C.
Upon CO exposure, a change is observed as a decrease in resistance for the $V_2O_5$ tested at 400°C but when exposed to CO at 25°C, this change is not observed as shown in Figure 3.15. In summary, this $V_2O_5$ device does not show a change in resistance to CO at 25°C and hence would not show any interference to CO at ambient conditions indicating the viability of this material for ambient NO monitoring.

3.6.5. Viability as a Gas Sensor

3.6.5.1. Device selectivity

Resistance changes to other gases were also tested at 25°C and the results are summarized in Figure 3.16. Vanadium pentoxide is exposed to 500 ppm nitrogen dioxide, 1000 ppm carbon monoxide, 150 ppm ammonia and 2.5 ppm acetone. As observed, there is an increase and decrease in the $R/R_o$ dependent on the analyte gas with 500 ppm nitrogen dioxide showing the greatest change after nitrogen oxide.

3.7. Discussion

3.7.1. NO Interaction with Vanadium Oxide

There are two distinct resistance pattern changes with as-obtained $V_2O_5$ upon exposure to NO at room temperature. Since our goal is to develop an ambient condition NO sensor, our focus in this discussion is to use the data presented above to explain the low temperature behavior. These include the two sets of data shown in Figure 3.7 and Figure 3.8. There are four observations that are relevant from these two figures. First, exposure of NO at low concentrations (~ 15 ppm) leads to an increase in resistance (Figure 3.7, at point (A), there is an increase in resistance of the material, which decreases at point (C) to (D) as NO is replaced by air). This process is
repeatable, as is obvious from the three cycles shown from point (A) to point (E) in Figure 3.7. Second, high concentration ~ 500 ppm of NO leads to reverse of this process (Figure 3.7 points (E) –(O) and Figure 3.8 points (A) -(I)). Third, between the low and high concentration of NO, and vice versa, there are transition effects (e.g Figure 3.8, point (A) to (D) exposure to ~ 500 ppm NO at first also led to sharp increase in resistance, with the resistance continuing to increase in air. Figure 3.8, changing from 500 ppm to 15 ppm point (I) to (K), there is a decrease in resistance). Fourth, for the same oxygen/nitrogen background, the resistances are quite distinct (points (D) and (I) in Figure 3.7 and points (G) and (L) in Figure 3.8), before and after exposure to high concentrations of NO.

In the literature, V₂O₅ is typically considered a n-type semiconductor due to the presence of oxygen defects, which are formed upon high temperature treatments. However, for unheated samples, n-type semiconducting property could arise from the presence of V⁴⁺, a valence state that is observed in the XPS data (Figure 3.3) in the as-obtained V₂O₅. The observation that 15 ppm NO leads to an increase in resistance is related to the binding of conducting electrons forming a depletion layer resulting in reduced conductivity and the formation of NO⁻. It has been pointed out that NO/NO₂ have properties like oxygen in that they chemisorb and accept/donate electrons. The increase in resistance with NO is typical of an n-type semiconducting oxide response and similar observations have been made on sputtered V₂O₅ thin films with NO₂/10 % air, at 280 °C. Thin films of V₂O₅ show an increase of resistance with NO at 290°C with air as background, and were explained as NO₂, the reaction product withdrawing electrons from the n-type semiconductor. Other n-type semiconducting oxides also exhibit increases in resistance. For example, NO with WO₃ at 280°C [29,39]. Upon exposure to NO in the 2-10 ppm range, an increase in resistance was also shown for SnO₂ up to 150 °C [40].
The lowering of the resistance with introduction of air, as observed in Figure 3.7 after 15 ppm NO exposure (point (C) → (D)) is expected since the bound electrons are released. These surface interactions at room temperature for 15 ppm NO can be described by the following equation

\[ NO + e^- \rightarrow NO^- \]  
(2)

Secondly, with high concentration of NO, there is a decrease in resistance at point (I)→(J) in Figure 3.7 and (D)→(E) in Figure 3.8. Higher concentrations lead to increased NO\(^-\) formation, leading to greater depletion of the surface of electrons (dominant charge carriers). We propose that the increased NO chemisorption results in the formation of an inversion layer with holes becoming the majority charge carrier (p-type). Thus, switching between low and high concentration of NO has led to switch from n- to p-type conductivity. The electrical resistivity changes are determined by the bulk donor density. With high bulk donor density, n-type behavior is expected, whereas with low bulk density, p-type behavior is expected. At intermediate donor densities, n → p or p → n transitions can be expected, depending on the amount and donor/acceptor properties of the adsorbing gas. It has been recognized that the n → p or p → n transition can be brought about by changes in the elemental composition (e.g. valence) as well as by altering the extent of chemisorption by an adsorbed gas, the latter phenomenon being observed here [41]. Another possibility for enhancing the inversion is the proposal that upon NO adsorption, there is dissociation to N\(_2\) and atomic oxygen at 250°C, with the oxygen diffusing into the semiconducting metal oxide and binding electrons [42] thereby enhancing the formation of the inversion layer. This process is unlikely under ambient temperature conditions.

There are several reports in the literature with similar observations. For Bi-doped SnO\(_2\), at a temperature of 310 °C, the resistance increased from 0 - 25 ppm NO\(_2\), followed by a decrease at concentrations of 25 - 50 ppm. With Al\(_2\)O\(_3\) - ZnO - V\(_2\)O\(_5\), there is a decrease in resistance from 0
- 240 ppm NO, followed by an increase up to 1200 ppm, though in all cases $R_{\text{air}}/R_{\text{NO}}$ exceeds 1.

In this study ZnO is considered n-type, whereas V$_2$O$_5$ is p-type.

Third observation is what we call the transition region, with 500 ppm NO, there is a rapid initial rise in resistance shown at point (E) → (F) in Figure 3.7 (and points (A) → (B) in Figure 3.8) which is expected since increasing NO chemisorption will lead to larger electron depletion in the surface layers. After the initial increase in the resistance, once air is introduced at point (H), (Figure 3.7) the resistance continues to increase to point (I), contrary to what would be expected if NO is simply desorbed, releasing the electrons to V$_2$O$_5$ (as observed with 15 ppm NO).

We propose that NO is strongly adsorbed on the V$_2$O$_5$ as NO$^-$ and the material is in a state of n to p inversion. In this state, as oxygen is introduced, it replaces the NO and the electrons released neutralize the holes, and the resistance increases. However, after steady state is reached (point (I) in Figure 3.7 and point (D) in Figure 3.8), there is still NO$^-$ strongly adsorbed to the surface, that is the oxygen does not replace all the NO. As the NO is repeatedly introduced, the adsorption slightly increases, resulting in the increase in the baselines (points (G) and (L) in Figure 3.7 and Figure 3.8, respectively). This explains why the baseline resistance is different on samples exposed to oxygen after exposure to low and high levels of NO. Thus, with exposure to high NO, the material is different as compared to samples exposed to low NO concentrations (~15 ppm), explaining the significant baseline differences with air prior and after exposure to high NO.

This interaction is probed by DRIFTS and no intermediate were observed on V$_2$O$_5$ at 25°C as observed in Figure 3.17. The surface of V$_2$O$_5$ at 25°C is exposed to 21% Oxygen for 1 hr as shown in Figure 3.17a then the sample is exposed to 1000 ppm NO shown in Figure 3.17b. A difference is then taken of the two spectra (Figure 3.17b - Figure 3.17a) to give Figure 3.17c which shows no intermediates formed on the surface for V$_2$O$_5$ at 25°C. There are several
substrates reported in the literature on which the NO is strongly adsorbed and not released upon exposure to oxygen, examples being SWNT [40] and metal ion exchanged zeolites [43].

The other transitional change is observed when there is a change from high to low concentration of NO (Figure 3.8, point (G) → (J)), where the system reverts back to the n-type, as the adsorbed NO is gradually released, upon repeated exposures to low levels of NO and oxygen. With the introduction of 15 ppm NO (point I), the NO adsorbs at the oxygen sites, releasing the O₂, as shown in Figure 3.8. The resistance decreases indicating still the presence of the inversion layer. With air, the resistance increases as expected for a sample with an inversion layer, but then continues to decrease, point (K) in Figure 3.8. At the low NO concentration 15 ppm, the NO⁻ does not generate an inversion layer. With further cycles of low NO and air(L) → (M) → (N) → (O), the sample returns to its native form resulting in characteristic increase of resistance with NO.

These types of transformations have been reported in other materials. For example, TiO₂ nanofibers [44], typically considered an n-type material, exhibits an increase in resistance with NO₂, but, at concentration ≥ 12.5 ppm, the resistance increased (almost a spike) followed by a decrease, and was explained due to n to p inversion induced by NO₂. For n-type Pd/WO₃ [4] and Cd-doped SnO₂ thin films [45], similar increase followed by decrease in resistance was observed. In the Pd/WO₃ system, there is an increase in resistance with the introduction of NO₂, followed by a decrease. The increase in resistance was attributed to the removal of charge carriers by the formation of NO₂⁻, and the decrease is due to desorption of oxygen species which release charge carriers to the film. With Cd-doped SnO₂, upon introduction of 10 ppm NO, there is a conductance increase followed by a decrease which is attributed to an initial reaction with
ionosorbed oxygen and then a release of the trapped charge carrier resulting in a decrease in the resistance as depicted by the scheme in Figure 3.18.

Thus, the overall model for the change in resistance of V$_2$O$_5$ with NO under ambient conditions is the chemisorption of NO, and binding of the conduction electrons. With high enough concentration of NO, the binding of the electrons leads to inversion at the surface, with the majority carrier becoming holes.

The data on VO$_2$ at room temperature as shown in Figure 3.12 and Figure 3.13 supports the model. There is a rapid increase in resistance which is proposed to occur by the same mechanism observed in equation 2. However, at high concentrations inversion is not observed since there are more conducting electrons (higher bulk donor density than the V$_2$O$_5$) present on the surface of the VO$_2$ sample.

As shown in Figure 3.9 as the V$_2$O$_5$ material is heated and exposed to low ~15ppm NO there is a conversion observed from an increase in resistance at temperatures <350°C to a decrease in resistance observed at temperatures >350°C. At room temperature, a resistance increase is observed indicated with R/R$_o$ > 1.0 in Figure 3.11 and at temperatures >350°C a decrease indicated by R/R$_o$< 1, which is more typical of a reducing gas. At intermediate temperatures, a gradual transition is observed with R/R$_o$ varying from greater than one to less than one. This is found to be reproducible and can be explained by the changes in oxygen reactivity on the surface of V$_2$O$_5$ at temperatures greater than 300°C. As the sample is heated, there is loss of oxygen from the framework leading to higher n-type bulk conductivity, and therefore the inversion is less of an issue. The increase of n-type carriers is also evident from observations that V$^{4+}$ occurs on V$_2$O$_5$ at elevated temperatures [24].
Thus NO oxidation to NO$_2$ [29] will occur using chemisorbed oxygen species thereby resulting in a decrease in resistance by withdrawing electrons from the n-type semiconductor. Thus the exposure of NO to V$_2$O$_5$ at elevated temperatures leads to a decrease in resistance and can be described by the following reactions.

$$NO + O^-_{ads} \rightarrow NO_2^- \quad (3)$$

$$NO_2^- \rightarrow NO_2 + e^- \quad (4)$$

With the 500 ppm NO, a resistance decrease is observed with NO at all temperatures. However, the mechanism of the resistance change occurs from different effects. Under ambient conditions, NO chemisorption leads to inversion, whereas at higher temperatures, reactions (3) and (4) are proposed to occur.

Further confirmation of the role of heating on $O^-_{ads}$ for the high temperature experiments is evident with the interaction of CO with V$_2$O$_5$ at 400°C as shown in Figure 3.14, which shows a decrease in resistance, similar to the NO data. The resistance decrease is based on reactions such as (3) and (4), and with CO$_2$ being the reaction product. Previous studies have noted that n-type semiconductors, such as Al$_2$O$_3$-V$_2$O$_5$, NO, NO$_2$ and CO all exhibited a decrease in resistance at temperatures of 400 °C [31].

3.7.2. Viability of V$_2$O$_5$ as An Ambient Gas Sensor for NO

The studies described in this chapter suggest that V$_2$O$_5$ is a good candidate for ambient temperature detection of NO and that the mechanism is driven by effective NO chemisorption. This property of NO distinguishes it from other molecules, such as CO, hydrocarbons, organic molecules and ammonia that cannot abstract electrons at ambient temperatures. At higher temperatures, many of these analytes lead to resistance changes due to reaction with adsorbed
oxygen, and has been reported previously. The inversion from n- to p-type switch from low to high concentration of NO is a complication from a sensing point of view.

3.8. Conclusion

It is interesting to contrast the CO sensor using RuO$_x$(OH)$_y$ and NO sensor using V$_2$O$_5$. In the former case, it is a chemical reaction catalyzed by the Ru that results in the sensing response, whereas for the latter, it is chemisorption that is controlling the response. However, in both cases, the presence of lower oxidation states of the metal are relevant. For the CO, it facilitates the oxidation, whereas with NO, it promotes the conductivity and the electrons involved in the chemisorption.
References


Table 3.1 Conductive metal oxide candidates for low temperature gas sensing and their properties

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Conductivity</th>
<th>Electron configuration</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO$_2$</td>
<td>Metal</td>
<td>d$^4$</td>
<td>Rutil</td>
</tr>
<tr>
<td>VO$_2$</td>
<td>Metal-Semiconductor</td>
<td>d$^1$</td>
<td>Distorted rutile</td>
</tr>
<tr>
<td>ReO$_2$</td>
<td>Metal</td>
<td>d$^3$</td>
<td>Distorted rutile</td>
</tr>
<tr>
<td>OsO$_2$</td>
<td>Metal</td>
<td>d$^4$</td>
<td>Rutil</td>
</tr>
<tr>
<td>NbO$_2$</td>
<td>Metal-Semiconductor</td>
<td>d$^1$</td>
<td>Tetragonal (rutile like)</td>
</tr>
<tr>
<td>IrO$_2$</td>
<td>Metal</td>
<td>d$^5$</td>
<td>Rutil</td>
</tr>
<tr>
<td>WO$_2$</td>
<td>Metal</td>
<td>d$^3$</td>
<td>Monoclinic at 25°C</td>
</tr>
<tr>
<td>PtO$_2$</td>
<td>Metal</td>
<td>d$^6$</td>
<td>Rutile like</td>
</tr>
<tr>
<td>RhO$_2$</td>
<td>Metal</td>
<td>d$^5$</td>
<td>Rutil</td>
</tr>
<tr>
<td>TcO$_2$</td>
<td>Metal</td>
<td>d$^3$</td>
<td>Distorted rutile</td>
</tr>
<tr>
<td>MoO$_2$</td>
<td>Metal</td>
<td>d$^2$</td>
<td>Distorted rutile</td>
</tr>
</tbody>
</table>
Figure 3.1 SEM of vanadium pentoxide (V_2O_5)
Figure 3.2. Diffraction pattern of vanadium pentoxide (V₂O₅)
Figure 3.3. XPS of vanadium pentoxide (V$_2$O$_5$)
Figure 3.4 SEM of vanadium dioxide (VO$_2$)
Figure 3.5 XRD of vanadium dioxide (VO₂)
Figure 3.6. XPS of vanadium dioxide (VO₂)
Figure 3.7. Room temperature test of vanadium pentoxide ($\text{V}_2\text{O}_5$) with 15 ppm NO then 500 ppm NO in 21% oxygen
Figure 3.8. Room temperature test of vanadium pentoxide ($V_2O_5$) with 500 ppm NO then 15 ppm NO in 21% oxygen
Figure 3.9. Effect of heat treatment on resistance change to 15 ppm NO on vanadium pentoxide ($\text{V}_2\text{O}_5$)
Figure 3.10. Effect of heat treatment on resistance change to 500 ppm NO on vanadium pentoxide (V$_2$O$_5$)
Figure 3.11. Summary of vanadium pentoxide (V$_2$O$_5$) heat treatment and resistance changes with the interaction of 15 ppm and 500 ppm NO.
Figure 3.12. Effect of heat treatment on resistance changes to 15 ppm NO on vanadium dioxide (VO$_2$) in 21% oxygen
Figure 3.13. Effect of heat treatment on resistance changes to 500 ppm NO on vanadium dioxide (VO$_2$) in 21% oxygen.
Figure 3.14. Vanadium pentoxide ($V_2O_5$) at 400°C exposed to 15 ppm and 500 ppm NO in 21% oxygen
Figure 3.15 Selectivity of Vanadium pentoxide, (V$_2$O$_5$) to carbon monoxide at 25°C and 400°C
Figure 3.16. Selectivity study on vanadium pentoxide ($V_2O_5$) at 25°C in 21% oxygen
Figure 3.17 Diffuse reflectance infrared difference spectra of vanadium pentoxide (V$_2$O$_5$) (a) surface exposed to O$_2$ (21%) exposure (b) O$_2$ (21%) and NO (1000 ppm) and (c) Difference between (a) and (b)
Figure 3.18 Scheme modified from reference [41] showing energy-level diagram of an n-type semiconductor (a) dry nitrogen atmosphere, which corresponds to a flatband situation (b) Oxygen adsorption leads to the surface states which are occupied by the electrons, this results either in a depletion layer and reduced n-type surface conductivity (c) or in an inversion layer (the Fermi level $E_F$ lies below the intrinsic level $E_i$) and p-type surface (Donor Levels not shown).
CHAPTER 4 FUTURE DIRECTIONS: SENSOR PERFORMANCE/MECHANISM

The studies presented in this thesis focus on understanding the interaction of carbon monoxide (CO) on hydrous ruthenium oxide and the interaction of nitric oxide (NO) on vanadium pentoxide. The potential of such systems for ambient temperature sensing have been demonstrated. However in order to design practical sensors, significant improvements in sensitivity and response times are required for the ruthenium oxide system. For the vanadium oxide besides the improvement in sensitivity to NO and response time improvements, information relating to the sensing mechanism is required.

4.1. Hydrous Ruthenium Oxide

4.1.1. Optimization of Porosity

In the improvement of hydrous ruthenium oxide for gas sensing applications, the increase of the porosity of the films used for resistance measurements are proposed by the following methods

4.1.1.1. Particle Size

The synthesis of particles <10 nm by other methods [1] would increase the porosity of the films. Thus smaller particles would result in larger areas of the material exposed for the possible interaction of CO.

4.1.1.2. Supercritical Drying
Optimization of the supercritical drying process by control of the materials deposition, exchange solvent/solvents to minimize shrinkage can be further explored to increase the porosity of the films. In the study of the interaction of CO on hydrous ruthenium oxide the thickness of the film used was determined to have an effect on the response times especially the films made by supercritical drying.

4.1.1.3. *Surface Area Measurements*

The surface area of the hydrous ruthenium oxide before and after air drying and supercritical drying will need to be properly quantified. Then the changes in surface area can be properly correlated to the changes observed in the resistances of the material.

4.1.2. *Catalytic Reactions*

Catalysts like gold [2] have been shown to facilitate the oxidation of carbon monoxide to carbon dioxide and facilitate the release of carbonate intermediates at room temperature. These catalysis reactions can be incorporated with the hydrated ruthenium oxide material to improve its sensitivity to carbon monoxide at room temperature.

4.1.3. *Mechanistic Studies: Role of water*

The exact role of water in the performance of the hydrous ruthenium oxide is not fully understood. Studies to determine the role of the water of hydration on the hydrous ruthenium oxide without changing the morphology of the oxide material would further assist in the understanding of the mechanism for the resistance change. A dehydration experiment on a vacuum line (10^-5 T) or by using a lyophilizer (20 x 10^-3 T) would remove significant amounts of
water from the material without changing the morphology of the material or reducing the surface
area.

4.2. Vanadium Pentoxide

4.2.1. Increase Porosity

4.2.1.1. New Synthesis
The vanadium pentoxide used in this study was used as received (5 µm) and so different
synthetic routes such as sol-gel methods are proposed to make smaller porous particles [3]. An
increase in porosity and open nano structure would lead to an increased surface area and more
sites for the possible interaction of NO on the surface of the material.

4.2.1.2. Supercritical Drying
Supercritical drying can be used to maintain the integrity of the gels formed by the synthesis of
vanadium pentoxide. The porous nature of these gels would provide a platform to increase the
interaction of NO on vanadium pentoxide and improve the sensitivity and response times.

4.2.1.3. Surface Area Measurements
The effect of the new synthesis and supercritical drying will be determined by correlating the
changes in surface area to the changes observed in the sensitivity of the material. A surface area
determination method such as BET (Brunauer. Emmett and Teller) can be used to for this.

4.2.2. Molecular Mechanism Determination
A study of the molecular interaction of NO on the surface of vanadium pentoxide would
facilitate the understanding of the mechanism for the resistance changes observed in the material.
Infrared spectroscopy can be used to probe the surface as the chemisorption progresses. The reaction products can also be monitored to capture the entire process.

4.2.3. Sensor Performance

Catalysts such as platinum [4] can be incorporated onto the vanadium pentoxide films to enhance the interaction of the films with NO. This could lead to improved sensitivity and decrease the detection limits from ppm to ppb NO at room temperature.
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