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Novel High Temperature Materials for *In-Situ* Sensing Devices

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Abstract:

The overriding goal of this project was to develop gas sensor materials and *systems* compatible with operation at temperatures from 500 to 700 °C. Gas sensors operating at these temperatures would be compatible with placement in fossil-energy exhaust streams close to the combustion chamber, and therefore have advantages for process regulation, and feedback for emissions controls. The three thrusts of our work included investigating thin film gas sensor materials based on metal oxide materials and electroceramic materials, and also development of microhotplate devices to support the gas sensing films. The metal oxide materials NiO, In₂O₃, and Ga₂O₃ were investigated for their sensitivity to H₂, NO_x, and CO₂, respectively, at high temperatures ($T > 500$ °C), where the sensing properties of these materials have received little attention. New ground was broken in achieving excellent gas sensor responses (>10) for temperatures up to 600 °C for NiO and In₂O₃ materials. The gas sensitivity of these materials was decreasing as temperatures increased above 500 °C, which indicates that achieving strong sensitivities with these materials at very high temperatures ($T \geq 650$ °C) will be a further challenge. The sensitivity, selectivity, stability, and reliability of these materials were investigated across a wide range of deposition conditions, temperatures, film thickness, as using surface active *promoter* materials.

We also proposed to study the electroceramic materials BaZr_(1-x)Y_xO_(3-x/2) and BaCe_(2-x)Ca_xS_(4-x/2) for their ability to detect H₂O and H₂S, respectively. This report focuses on the properties and gas sensing characteristics of BaZr_(1-x)Y_xO_(3-x/2) (Y-doped BaZrO₃), as significant difficulties were encountered in generating BaCe_(2-x)Ca_xS_(4-x/2) sensors. Significant new results were achieved for Y-doped BaZrO₃, including sensitivities of more than 60 atm⁻¹ for H₂O vapor at 400 °C. These results were achieved despite significant difficulties with a strong Ba deficiency in the deposited films, and difficulties with stress in the targets and films. Ultimately, these films achieved good sensitivity, selectivity, and reliability in our gas sensing tests.

The final thrust of our project was to develop microhotplates. We proposed the use of SiC thin films for the heater of the microhotplate, but despite extensive efforts we were not able to secure a reliable source of SiC. An alternative microhotplate architecture using SiO₂ and Si₃N₄ suspended membrane structures, and a polysilicon heater were developed, which could be fabricated at commercial MEMs foundries. These microhotplates were fabricated at Microtechnology Services Frankfurt (MSF) in Germany. The fabricated heaters were able to achieve temperatures > 600 °C using ~ 0.25 W, and when combined with In₂O₃ films demonstrated sensor systems with sensor responses up to 50 for 25 ppm NO_x, and time constants of less than 10 s.

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I. Executive Summary

The most important goals of this project was to extend the performance of thin film metal oxide and electroceramic gas sensing materials to higher temperature regimes ($T > 500\text{ }^{\circ}\text{C}$) through understanding their sensor mechanisms and characteristics. Sensors able to operate at temperatures from 500 to 700 $^{\circ}\text{C}$ are much more compatible with being placed in exhaust gas flows of fossil energy systems such as coal-fired power plants and diesel engines. The vast majority of research on metal oxide materials has focused on improving their sensitivity at low temperatures to make the sensors more energy efficient and useful for air quality monitoring, and emission monitoring further from the combustion chamber. No single sensing mechanism is able to distinguish the broad spectrum of species in typical combustion exhaust streams. We proposed to focus on the target gases of NO_x , NH_3 , H_2 , CO , CO_2 , H_2O , and H_2S , and to research and develop sensing *systems* for these gases compatible with high temperatures and harsh environments. The materials we investigated included NiO , In_2O_3 , and Ga_2O_3 for the metal oxide materials due to their high melting points, low vapor pressures, and at least reasonable gas sensitivities reported in the literature. We also proposed to study the electroceramic materials $\text{BaZr}_{(1-x)}\text{Y}_x\text{O}_{(3-x/2)}$ and $\text{BaCe}_{(2-x)}\text{Ca}_x\text{S}_{(4-x/2)}$ for their ability to detect H_2O and H_2S , respectively. In conjunction with investigating the gas sensing properties of these materials, we also proposed to develop SiC based microhotplates to support and control the temperature of the sensitive films, and enable the integrated sensors to tolerate harsh environments.

We have very exciting results to report for most of the materials investigated, and have learned a great deal about the basic sensing mechanisms that operate at high temperatures. In general, we have investigated the physical, structural, electronic, and gas sensing properties of these materials, focusing on temperatures from 500 to 650 $^{\circ}\text{C}$. We measured their gas sensitivity, selectivity, and stability to compare these results with those reported in the literature for lower temperatures. For the metal oxide materials, we were able to achieve excellent sensitivities (gas sensor responses > 10) for temperatures up to 600 $^{\circ}\text{C}$. While these results are very exciting, the definite trend in sensor responses for temperatures greater than 500 $^{\circ}\text{C}$ is towards lower sensor responses. Put another way, the activation energy (E_a) for the gas sensing properties are negative at these higher temperatures. We suspect that this might result from the gas desorption kinetics for these types of sensors. We believe these results will be very important for guiding further research to extend the capabilities of this class of gas sensing materials to higher temperatures.

A similar decline in sensitivity at high temperatures was also observed for $\text{BaZr}_{(1-x)}\text{Y}_x\text{O}_{(3-x/2)}$, though its sensing mechanism was based on absorption and ionic conduction. The conduction mechanisms for the electroceramic materials are more complex, as they involve electrons, holes, protons, and oxygen ions, each of which is affected differently by temperature. We believe that the lower sensitivities at very high temperatures result from conduction modes besides proton conduction, which is needed to sense H_2O , becoming dominant at these temperatures, resulting in lower sensitivities for H_2O . Again, despite these trends towards lower sensitivity as temperatures exceed 600 $^{\circ}\text{C}$, we are still very excited to report that reasonable sensitivities ($> 60\text{ atm}^{-1}$) have been achieved, particularly for the thinnest films (50 nm thick).

We were also able to make significant progress on the third aspect of our project, which was harsh environment compatible microhotplates. The 3rd generation microhotplates, which used SiO_2 and Si_3N_4 membranes, and polysilicon heaters, were able to achieve temperatures $> 600\text{ }^{\circ}\text{C}$, using less than $\frac{1}{4}$ Watt of power, and were shown to enable gas sensing measurements in data presented below. The one aspect of the proposed microhotplates that we were not able to accomplish was the use of SiC as the heater material. Despite extensive outreach efforts to

established SiC researchers, former colleagues, and requests to the few companies that have fledgling efforts in 3C and thin film SiC, we were not able to source material of sufficient quality and consistent electrical properties for use in our microhotplates. We continue to feel that SiC offers tremendous advantages for harsh-environment microhotplates, and will continue to work on realizing SiC-based microhotplates as means to conduct this work become available. One benefit of the design that we did design, simulate, and fabricate is that it utilizes a SiO_2 and Si_3N_4 membrane structure, therefore these designs are compatible with production at many MEMS foundries, making this a viable platform for the future. Also, In_2O_3 films were deposited on the fabricated microhotplates, and were found to have excellent sensor response (up to 50) and sensor response speed (≤ 10 s) during testing with NO_x . These results suggest that the microhotplate design warrants further attention to determine its potential for commercialization.

The following paragraphs give a high-level overview of the important results that have been achieved during this project for the individual materials that were investigated. Also, details of the custom-built gas sensor test station that was used for all the gas sensor testing are included in this report as an appendix which contains Clayton Butlers Master's thesis. In addition, a summary of our performance on the project milestones is presented in Section III.

Our research on NiO films has focused on their H_2 sensing properties, particularly for larger concentration of H_2 (500 to 10,000 ppm). Also note that unlike measurements for most other materials presented in this report, synthetic air was used as the carrier gas for testing the gas sensitive properties of NiO. It is important to note that based on the sensing mechanism for NiO, the presence of an oxidizing gas was important for achieving reliable gas sensor responses. To our knowledge, some of our achieved gas sensor responses (> 175 for 5,000 ppm H_2) at operating temperatures of 400 °C are some of the best results report in the literature. In addition, little or no research in the literature has addressed use of NiO sensing films at temperatures > 500 °C. As was stated previous, the gas sensitivity of our films did steadily decrease from their maximum sensitivity at 400 °C. We hope this situation can be improved through the use of promoter layers, as those have demonstrated exceptional results when used in conjunction with In_2O_3 as will be described below. The selectivity of NiO for H_2 was found to be good compared with NO_x , NH_3 , and CO_2 as its sensitivity to these individual gases was significantly lower than for H_2 . This situation changed dramatically when mixtures of these gases were combined with the H_2 test gas. For NO_x and NH_3 in particular, the presence of small concentrations (< 300 ppm) dramatically decreased the sensor response to H_2 . Similar effects were observed for other metal oxide materials which are likely due to gas and surface reactions, and are important to note as we progress towards deploying true sensor systems in complex exhaust streams.

Work on In_2O_3 films examined their NO_x sensing characteristics in a wide range of conditions. The effects of deposition conditions, use of promoters (*e.g.* Au and TiO_x layers less than 5 nm thick), operating temperature, carrier gas, film thickness, and many other variables were investigated. Just the deposition conditions were found to have a very large effect on the sensitivity of these films to NO_x , and films deposited in sputtering ambients with 10 to 25% O_2 were found to have much better sensing characteristics than those deposited in pure Ar. In addition, the use of Au promoter layers was found to significantly improve the sensitivity, and also improve the time constants for the response to the test gases. Promoters also influenced how temperature affected the gas sensitivity, and did lessen the trend towards lower sensitivities at high temperatures, but certainly did not eliminate it. In addition, a variety of selectivity experiments were conducted. Similar to NiO results, the In_2O_3 films showed little sensitivity to NH_3 and CO_2 , but did show some sensitivity to H_2 , each in N_2 carrier gas. When the sensor was

exposed to mixtures of NH_3 and NO_x , the NO_x sensitivity went down dramatically, which is incongruent with its low sensitivity to only NH_3 . This effect can result from gas-phase reactions, where the NH_3 reduces the NO_x , and also might involve surface chemistry and controlling surface adsorption sites. Understanding this better will be important for use of In_2O_3 sensor in selective catalytic reduction (SCR) applications. Also note that H_2 containing test gases were found to etch In_2O_3 films at temperatures $> 500^\circ\text{C}$. TiWO_x were not found to be etched in H_2 containing test gases, and also had excellent NO_x sensitivities, so warrant significant further research.

Gas sensors based on Ga_2O_3 were proposed for use as a CO_2 sensing material, a gas which is very challenging to detect. Ga_2O_3 films were deposited using different deposition conditions, and some films were also annealed afterwards to investigate the effects of temperature and ambient on the physical, electronic, and gas sensing properties of the films. Only very modest sensitivity to CO_2 was achieved in gas sensor tests, therefore we decided to test them for H_2 sensitivity, as this is often a strength for *n*-type metal oxide sensors. While stronger sensitivities were found for H_2 , we also determined that exposure to H_2 containing test gases at typical operating temperatures etched the Ga_2O_3 , similar to what occurred in In_2O_3 thin films. Thinner films deposited at slightly higher pressures did tend to have the best sensing characteristics of tested devices, and annealing in pure N_2 was also found to contribute to some of the best sensitivities measured.

The electroceramic material $\text{BaZr}_{(1-x)}\text{Y}_x\text{O}_{(3-x/2)}$ was investigated as a high temperature H_2O vapor sensing material. Targets of this material were initially hard to obtain, due to cracking of the targets during fabrication. Films were deposited by both sputter deposition and pulsed laser deposition. In all cases, the films were deficient in Ba concentration. Some were extremely deficient (75% lower than the target stoichiometry). Significant effort was expended to optimize the film composition to match bulk compositions for which prior sensitivity data was available. With optimized deposition processes, we demonstrated good sensitivity ($> 60 \text{ atm}^{-1}$), selectivity, and stability for these materials, suggesting they are a viable candidate for a commercial sensor. Film stress and the contact metallization were also found to be important for realizing good sensors. Many of the deposited films crack with annealing, in a mud-flat cracking mode, which indicates the films were under tensile stress. Different substrate materials and achieving a more stoichiometric Ba concentration might help resolve this. Also, we found the contact metallization to be very important for sensor functionality. Initially, films were deposited on top of the IDE contact metallization, and this did not allow gas exchange at the contact, which is critical for electroceramic sensors. Top contacts were investigated, and Au contacts with a Cr adhesion layer were found to give the best sensor response.

II. Work Performed during the Reporting Period

II. A. Metal Oxide Materials

Description/Rationale

This project thrust focuses on investigating new metal oxide semiconductor materials as gas sensitive layers at temperatures greater than 500°C . Use of these materials and mechanisms for their response to the target gases has not been well investigated in the high temperature regime. The materials investigated include In_2O_3 , Ga_2O_3 , and NiO , as well as promoter materials which will improve the selectivity and/or sensitivity of the metal oxide materials to different gases.

Results and Discussion

Part I: NiO thin films

Nickel oxide (NiO) films were deposited on fused silica substrates in a Perkin-Elmer 4400 sputtering system from an 200 mm NiO target (99.995 % pure), with a sputtering ambient of Ar at 10 mTorr, and a RF power of 500 W, yielding a deposition rate of ~18.9 nm/min. NiO films were then annealed at 900 °C in synthetic air (80% N₂, 20% O₂). We present data on the structure, surface morphology, and chemical composition of 30 to 130 nm thick NiO films using X-ray diffraction (XRD), Atomic Force Microscope (AFM), and X-ray photoelectron spectroscopy (XPS), respectively. This report includes, gas sensor responses at temperatures from 300 to 650 °C for H₂ test gas concentrations ranging from 500 to 10,000 ppm in a synthetic air carrier gas.

After annealing, the 50 nm thick films showed the highest surface roughness of 14.6 nm and the highest gas sensor response at all operating temperatures tested. Surface roughness and area appear to be correlated to the gas sensor response of NiO. An average gas sensor response of 55 was found at 600 °C with a standard deviation of 6.23. Repeatability measurements for gas sensitivity were collected at 600 °C for 8 hours where NiO was exposed to H₂ 11 times at concentrations varying from 500 to 10,000 ppm and each exposure lasted for 20 minutes. Cross sensitivity was investigated in gas mixtures containing 1,100 ppm CO₂, 150 ppm NH₃ and 50 ppm NO_x. Selectivity was observed to decrease as the operating temperature increased.

Introduction

In this report we present the microstructure, surface morphology, film composition, and the gas sensitivity properties of NiO films measured by XRD, AFM, XPS and custom-build gas sensor test station, respectively. To date, gas sensor response, repeatability and selectivity are the main performance characteristics of MOX gas sensors¹. Most MOX gas sensors are sensitive to a variety of different gases, making selectivity a challenge^{2,3}. Gas sensor response tests were carried out at operating temperatures from 300 to 650 °C for H₂ (500 to 10,000 ppm) in synthetic air carrier gas. H₂ selectivity was investigated using gas mixtures and also individual gases that are relevant ranges in exhaust gas emissions⁴ of 5,000 ppm H₂, 150 ppm NH₃, 1,100 ppm CO₂ and 50 ppm NO_x. We also investigated the repeatability of NiO films for sensing H₂. The gas sensor response was calculated by the change in resistance divided by base line resistance:

$$GSR = \frac{R_g - R_0}{R_0} \quad (1)$$

R₀ denotes the base line resistance of the sensor before gas exposure, R_g denotes the resistance during gas exposure.

Experimental

NiO thin films were deposited by radio frequency (RF) sputter deposition from an 200 mm ceramic NiO target. Deposition parameters were kept constant at 10 mTorr and 500 W in an Ar atmosphere, and fused silica was used as substrate material. Sensitive layers were deposited on test structures consisting of interdigitated electrodes (IDE) with 10 finger pairs and 100 µm finger spacing (see Fig. 1).

Fig. 1. Test structure schematic including integrated electrodes (IDE) test structures for electrical characterization and resistive temperature device (RTD)⁵.

The IDE structure was used to measure the change in film resistance. All films were annealed at 900 °C in synthetic air (20% O₂, 80% N₂) for 5 hours. An XRD investigation was carried out with a Cu K_α with an acceleration voltage of 45 kV and an emission current of 40 mA. The dwell time and step size were 0.4 sec and 0.01°, respectively. AFM analysis was carried out with a Veeco Dimension3000 AFM in tapping mode with etched Si tips (tip radius 5 nm). XPS characterization was performed using a Kratos Axis ULTRADLD system applying monochromatic Al K_α radiation. All gas measurements were carried out on a custom-built gas sensor test station⁶. Sensors were tested at operating temperatures from 300 to 650 °C and with different layer thicknesses to determine their effect on the sensing properties of NiO films in order to find the most sensitive NiO structure. The goal of this research was to investigate gas sensitive behavior at high temperature; therefore, most characterization was carried out at 600 °C. Repeatability measurements were performed at 600 °C for 8 hours. Selectivity to H₂ was found to decrease with increasing temperature in a gas mixture of NO_x, CO₂ and NH₃.

XRD Results

XRD spectra were collected from annealed NiO films as function of thickness from 30 to 130 nm and presented in Fig. 2. None of the as-deposited films revealed diffraction peaks, indicating they are amorphous structures. Annealing the sputtered layers resulted in a slight crystallization of the films to become weakly polycrystalline. The 80 and 130 nm annealed samples had a (111) reflection which indicates a slightly textured polycrystalline structure. These peaks were weak resulting from a combination of very thin films and only moderate crystallization. Experiments could not distinguish between rhombohedral NiO and cubic NiO bunsenite, because the peaks for both phases are very close. The diffraction peak for cubic (111) NiO in Fig. 2 is at $2\theta = 37.594^\circ$ (dashed line). According to the JCPDS database, rhombohedral NiO shows a diffraction peak at $2\theta = 37.248^\circ$. The X-ray diffraction peak is shifted from the position expected by the

NiO bunsenite JCPDS database ($2\theta = 37.281^\circ$), which is likely due to compressive stress in the out-of-plane direction. Since only one diffraction peak was observed, we cannot determine whether this involves cubic or rhombohedral NiO.

Fig. 2. XRD spectra of a 30, 50, 80 and 130 nm annealed NiO films. Measured data were offset by an intensity of 50. Weak (111) peak reflections were observed for the 130 and 80 nm films, respectively.

Surface morphology

The surface morphology was characterized as a function of film thickness by AFM before and after annealing (see Fig. 3). In addition to reducing film defects and slightly crystallizing some films, the annealing process is also important to stabilize the films for future tests. The sensitive layer should not change its film properties due to high temperatures or exposure to test gases, which would be likely for unannealed films.

Fig. 3. AFM micrographs were taken from a $1 \times 1 \mu\text{m}^2$ area. The as deposited films (a-d) are shown with a 10 nm scale bar, and all annealed films (e-h) are shown with a 100 nm scale bar. Sample a), b), c) and d) show AFM scans for as deposited 30, 50, 80 and 130 nm thick films, respectively. Sample e), f), g) and h) show AFM scans of 30, 50, 80 and 130 nm thick annealed films.

As deposited films show an increase in surface roughness with layer thickness (see Fig. 4). We saw a dramatic increase in surface particle size for all analyzed layer thicknesses after annealing. All annealed NiO samples appear to form a hillocked morphology. The calculated RMS roughness also increased for all films after annealing. The 50 nm annealed NiO films showed the highest RMS roughness (14.6 nm). The surface areas for the annealed films were also calculated and are presented in Table 1. These are surface areas of a $1 \times 1 \mu\text{m}^2$ area, therefore any surface area greater than $1 \mu\text{m}^2$ results from surface topography. In Table 1, the 50 nm thick annealed films have the largest surface area of $1.127 \mu\text{m}^2$, which is $\sim 13\%$ more surface area than an ideal flat surface. We observed the highest response for the 50 nm thick films. This is consistent with models that suggest high surface area films have more absorption sites⁷ for the target gas and have more particle boundaries that can have chemisorbed gas species and their affect on the film resistivity⁸.

Fig. 4. RMS roughness (R_{RMS}) as a function of layer thickness for as deposited and annealed NiO films. Note that the annealed 50 nm film is dramatically rougher than the substrate.

Table 1. Surface area as a function of layer thickness after annealing for 5 hours in synthetic air.

Layer thickness (nm)	30	50	80	130
Surface area (μm^2)	1.044	1.127	1.096	1.042

Chemical composition

Survey and high-resolution spectra were collected from annealed samples both before and after Ar ion beam etching. A slightly oxygen-rich stoichiometry gives NiO its *p*-type character⁹. XPS measurements before etching show an excess of oxygen (see Table 2). After ion beam etching, XPS measurements indicate the film stoichiometry is nickel rich. The nickel rich stoichiometry may be caused by ion beam etching, through ion beam reaction of metal oxides, which has been reported for some materials.

Table 2. Film composition measured by XPS for 30, 50, 80 and 130 nm thick annealed NiO films before and after 120 seconds of Ar ion etching.

Atomic concentration before ion beam etching								
layer thickness [nm]	Ni	O	Ti	N	C	Ar	Si	Pt
30	17.31	52.16	30.53	0	0	0	0	0
50	10.06	41.82	0.96	0.83	29.13	0	12.95	4.23
80	32.88	45.62	2.9	0	17.18	0	1.4	0
130	13	45.48	2.44	0	35.79	0	3.29	0
Atomic concentration after ion beam etching								
30	62.59	35.68	0	0	0.59	1.14	0	0
50	52.72	39.5	0.14	0	1.54	0	5.6	0.5
80	58.6	37.6	2.55	0	1.26	0	0	0
130	63.7	32.98	0.54	0	1.74	1.04	0	0

Ion beam etching was carried out to remove the surface contaminants including adventitious carbon and adsorbed oxygen. The silicon signal comes from the fused silica substrate which also contributes to the oxygen, and platinum and titanium were part of the IDE metallization of the sensor.

Gas sensitive properties

The gas sensor response of annealed NiO films were investigated upon exposure to H₂, NH₃, NO_x and CO₂ test gases in synthetic air carrier gas (20% O₂, 80% N₂) for operating temperatures from 300 to 650 °C for all films. A custom-built gas sensor test station was used for all measurements⁶. The sensor resistance was measured every 0.6 sec by a Keithley 2700 digital multimeter and recorded using a computer. Sensors were placed on a heater chuck to maintain them at the desired operating temperature, and probe needles were used to contact the electrical bond pads. As a *p*-type semiconductor gas sensor, NiO reduces its resistance when exposed to an oxidizing gas such as oxygen. The mechanism for this effect is that chemisorption of oxidizing gases requires the transfer of an electron from the semiconductor to the adsorbed molecule. The decrease in electron concentration increases the hole concentration by mass action, and results in a higher carrier concentration. Also, the negatively charged adsorbed gas molecule creates surface band bending, which attracts higher concentrations of positively charged holes to

surfaces. Both of these effects increase the conductivity of the material. In the case of a reducing gas such as H_2 and NH_3 , the resistance of NiO increases because reducing gases react with adsorbed oxygen and remove it from the surface. Breaking the chemisorbed bond injects the trapped electron into the NiO film, which decreases the hole concentration, and lowers the accumulation of holes at the surface¹⁰. Consequently, the number of holes in the NiO is reduced, and the film resistivity increases.

Temperature dependence of NiO gas sensitivity

The gas sensing characteristics of the NiO films were measured at operating temperatures from 300 to 650 °C to determine the effect of temperature, and to investigate the mechanisms for the temperature dependence. The selectivity of the NiO films was also characterized as a function of operating temperature. Fig. 5 shows the gas sensor response for different NiO film thicknesses at different operating temperatures. We found 50 nm thick annealed NiO films to be most sensitive in the tested temperature range.

Before testing, each sensor underwent a *burn-in* process of 9.5 hours during which the sensors were exposed to 5,000 ppm H_2 four (4) times for 30 minutes at 600 °C. After the *burn in*, sensors were found to be more sensitive and have more repeatable sensor responses. Before each H_2 exposure, the sensor was maintained in synthetic air for 90 minutes. The gas sensor response of 30, 50, 80 and 130 nm annealed NiO films was tested with 5,000 ppm H_2 for different operating temperatures. The gas sensor responses are plotted in Fig. 5, which were calculated from four H_2 exposures, each of which lasted for 30 minutes. Fig. 5 presents the measured gas sensor responses as a function of operating temperature, error bars are given over the full range. In this figure, there are only error bars for 50 nm NiO films, since the error for 30, 80 and 130 nm NiO were smaller due to lower gas sensor responses.

Fig. 5. The gas sensor response as a function of operating temperature for different layer thicknesses is plotted. The 50 nm thick film had the highest sensor response particularly from 400 to 600 °C.

Layers with a high surface area offered more surface sites for oxygen to absorb, from the gas phase⁹. The accumulation layer was caused by a negative charge on the surface and excess holes

near the surface¹¹. The accumulation layer has a higher conductivity compared to the bulk of the film the inside of a grain, which explains why we see the highest conductivity for all tested film thicknesses at 50 nm (see Fig. 6). The film resistivity was calculated using the equation

$$R = \rho \frac{l}{A \times n} \quad (2)$$

where ρ is the film resistivity ($\Omega \cdot \text{cm}$), R is the measured resistance (Ω), A is the cross sectional area of the film (cm^2), l is the distance between each interdigitated electrode (μm), and n is the number of interdigital electrode pairs ($n = 10$).

Fig. 6. Resistivity of NiO in carrier gas as a function of temperature and layer thickness. Resistivity was calculated in order to compare different layer thicknesses.

The 50 nm thick annealed NiO films were found to have the lowest sensor base line resistivity at all measured temperatures, which also correlates with the highest gas sensor response. For all tested temperatures, we found that 50 nm annealed films show the lowest resistivity followed by 80 nm samples. 30 and 130 nm thick annealed samples show the highest resistivity, which may be explained by their lower surface area. The 30 nm samples actually have a higher surface area, but we still see a higher resistance compared to 130 nm, which can be due to bulk resistivity. The accumulation layer has a higher conductivity compared to bulk and the inside of a grain. Having the highest surface area at 50 nm also implies that we have a higher accumulation layer volume. A higher volume density of accumulation region leads to more charge carriers and a lower resistance.

Repeatability

Repeatability is also a critical factor for commercial gas sensors. Commercialized products need to work over long periods of time without the need for recalibration or replacement. Instability of MOX gas sensors can be caused by changes in crystallite sizes caused by insufficient annealing, or irreversible reactions between gases and the surface, or through reactions with the substrate. Fig. 7 shows repeatability measurements of a 50 nm thick NiO film which was annealed at 900 °C for 5 hours in synthetic air operating at 600 °C. Each gas exposure

and gas recovery cycle lasted for 20 minutes. H₂ gas concentrations of between 500 and 10,000 ppm were tested.

Fig. 7. 50 nm thick NiO annealed at 900 °C in synthetic air, operating temperature 600 °C. Each gas exposure cycle and recovery cycle lasted for 20 minutes, and the concentrations of H₂ used are indicated by the blue line and secondary y-axis.

We found sensor responses to be fairly repeatable and stable throughout the tested time. The electrical resistance of a sensor is well correlated by the power law equation³

$$R = a \cdot P(H_2)^\alpha \quad (3)$$

We found that the gas sensor response at 600 °C can be fitted the power law and $\alpha = 0.6$. MOX gas sensors are expected to show a linear correlation between gas concentration and sensor response when plotted on a logarithmic scale¹².

Selectivity

Even though metal oxide gas sensors show high sensitivities towards their target gases, selectivity is a major challenge for these materials^{13,14}. We investigate the selectivity of 50 nm thick NiO films, since those films had the highest gas sensor response. Individual gas exposures of 50 ppm NO_x, 150 ppm NH₃, and 1,100 ppm CO₂ in synthetic air carrier gas did not large gas sensor responses compared to the H₂ response. In contrast, on exposure to a mixture of all tested gases, we see a *dramatic* reduction in sensor response compared to pure H₂ exposure. One explanation for the reduction in response is that gases compete with hydrogen for the available adsorption sites. Determination of the responsible gas was attempted by exposing NiO to hydrogen with one additional gas (see Fig. 9). Fig. 8 presents the response of NiO towards individual gases and towards a mixture of all gases at operating temperatures of (a) 500 and (b) 600 °C, respectively. From these two plots, we can see that selectivity towards H₂ decreases as the temperature increases.

Fig. 8. Shows the sensor response of a 50 nm thick NiO film that was operated at (a) 500 °C and at (b) 600 °C being exposed to 50 ppm NO_x, 150 NH₃, 5000 ppm H₂, to a mixture of all gases and again to 5000 ppm H₂.

NiO was not sensitive to CO₂, either as a test gas or mixture with H₂. NH₃ and NO_x both dramatically reduce the sensor response of NiO when mixed with H₂ test gases (see Fig. 9).

Fig. 9. Gas sensor response measurements from 50 nm NiO film exposed to 5000 ppm H_2 for each cycle, and additionally 50 ppm NO_x (2nd cycle), 150 ppm NH_3 (4th cycle), and 1100 ppm CO_2 (6th cycle).

Fig. 10. Gas sensor response of a 50 nm NiO film operating at 600 °C to 50 ppm NO_x and 150 ppm NH_3 in synthetic air carrier gas.

In Fig. 10, first note that the y-axis scale is significantly smaller than used to plot the H_2 responses. We can see the typical *p*-type behavior of NiO when exposed to the oxidizing gas NO_x , which is a reduction in resistance during exposure to 50 ppm NO_x . H_2 , NH_3 are reducing gases, which remove chemisorbed oxygen during exposures, thereby reducing the hole concentration increasing the resistance of the sensor. Fig. 10 not only shows that NiO reacts with different gases as specified by the sensing mechanism, it also shows its relatively low response towards NH_3 and NO_x for the tested gas concentration. As we saw in Fig. 9, 50 ppm NO_x as well as 150 ppm NH_3 are capable of reducing the sensor response by more than 50%. It may be the case that NH_3 and NO_x have a higher affinity to NiO than H_2 , which is why they

appear to have such an influence on sensor response in the presence of H_2 . Selectivity towards H_2 in the presence of NO_x was investigated at temperatures between 300 and 650 °C (see Fig. 12). Fig. 11 shows a representative gas sensor response measurement used to investigate the selectivity of NiO towards H_2 . Initial exposure to H_2 was carried out for 20 minutes. After a recovery time of 20 minutes, the sensor was again exposed to 5,000 ppm H_2 , but this time in the presence of 50 ppm NO_x . The sensor was exposed to H_2 for one hour while the NO_x concentration changed every 20 minutes. The NO_x concentration was increased from 50 ppm to 100, then to 300 ppm NO_x and finally, for the last 20 minutes, the NO_x concentration was reduced to zero. Fig. 13 shows the reduction in selectivity with increasing temperature while exposing the sensor towards 50, 100 and 300 ppm NH_3 .

Fig. 11. H_2 selectivity measurement while increasing the NO_x concentration.

Fig. 12. Relative gas sensor response as a function of temperature for a 50 nm thick NiO film (annealed). The red line indicates the gas sensor response of a sensor towards 5000 ppm. The blue, grey and green lines indicate the percentage of gas sensor response whilst adding 50, 100 and 300 ppm NO_x , respectively.

Fig. 13. Relative gas sensor response as a function of temperature for a 50 nm thick NiO film (annealed). The red line indicates the gas sensor response of a sensor towards 5000 ppm. The blue, grey and green lines indicate the percentage of gas sensor response while adding 50, 100 and 300 ppm NH₃, respectively.

Conclusions

We investigated 30, 50, 80 and 130 nm thick NiO films annealed at 900 °C for 5 hours in synthetic air. The 50 nm films were found to be most sensitive towards H₂ in synthetic air carrier gas for temperatures ranging from 300 to 650 °C. The highest surface roughness and surface area were found for 50 nm via AFM measurements. The speculation that electrical conduction for thin NiO layers takes place mainly in the accumulation layer are consistent with the resistivity measurements. 50 nm thick annealed NiO films were observed to have the lowest resistivity. Stability and repeatability measurements were performed at 600 °C for H₂ concentrations ranging from 500 to 10,000 ppm. The sensor response for different hydrogen concentrations was found to follow a power law relationship where $\alpha=0.6$. Selectivity to hydrogen was investigated in a gas mixture of 50 ppm NO_x, 150 ppm NH₃ and 1,100 ppm CO₂. In order to investigate the gas responsible for the reduction in sensor response, we exposed NiO to mixtures of hydrogen with only one additional gas. NiO was found to be selective in a gas mixture with CO₂. In a gas mixture of 5,000 ppm H₂ and 50 ppm NO_x or 150 ppm NH₃, we observed a sensor reduction of more than 50% in comparison with exposure to pure H₂. We found decreasing selectivity with increasing temperature in a mixture of H₂ and NO_x. The same phenomenon was observed in a H₂ and NH₃ gas mixture. Future work will focus on increasing the selectivity at higher temperatures, which may be achieved via promoter layers or chemical filters.

Part II: In₂O₃ thin films

RF Sputter Deposited In₂O₃ thin films

In₂O₃ thin films were RF sputter deposited on microhotplate structures with different thickness (40 to 300 nm) in pure Ar as well as Ar and O₂ (10% and 25%) mixture. In₂O₃ films without promoter layers and with gold or TiO_x promoter layers (~ 3 nm) were investigated for NO_x sensing. Some of the films (without promoters, Au and TiO_x promoter films) were also annealed at 900 °C in ambient of either N₂, O₂, 2% H₂ in Ar, or 50% O₂ in N₂ mixture to stabilize

the gas sensing properties of the In_2O_3 films and understand the effect of annealing conditions on the gas sensor response.

Effect of deposition conditions and film thickness

We investigated the effect of film thickness from 40 to 310 nm and deposition conditions using Ar, and Ar with 10% and 25% O_2 on the microstructure and electrical properties of these thin films utilizing XRD and resistivity measurements. Fig. 14 presents XRD spectra collected from In_2O_3 samples as a function of film thickness and deposition conditions. As the thickness of the In_2O_3 thin film increases, the intensity of the In_2O_3 (222) and (400) reflections increase. With addition of O_2 , broadening of the (222) peak occurs and the intensity of the (400) peak drastically reduces. Steffes has observed changes in the In_2O_3 texture from (111) to (211) phase resulted in a higher sensitivity to NO_2 ¹⁵. The (400) texture may influence the NO_x gas sensitivity for In_2O_3 films as we have observed films deposited in O_2 ambient have the highest NO_x response. The dotted lines resemble the In_2O_3 standard peaks from JCPDS files.

Fig. 14. X-ray diffraction spectra showing the effect of film thickness and deposition conditions on the crystalline structure of In_2O_3 thin films. Note the broadening of the peaks as well as absence/weak reflections of the (400) In_2O_3 structure in O_2 deposited samples.

Table 3 shows the resistivity of thin film In_2O_3 with different thickness and deposition conditions. Thinner films (~ 40 nm) have one order magnitude higher resistivity ($0.1 \text{ } \Omega\text{-cm}$) compared to In_2O_3 films thicker than 150 nm which have resistivity of $0.005 \text{ } \Omega\text{-cm}$. Films deposited in Ar with O_2 process gases had resistivities of ~ 10 to $35 \text{ } \Omega\text{-cm}$ which are much higher than those deposited in pure Ar ($\sim 0.005 \text{ } \Omega\text{-cm}$). Films deposited in either all ambients were indium rich with an approximate O/In ratio of 1.22 measured by XPS spectroscopy. In_2O_3

films deposited by reactive evaporation and reactive ion plating in literature have an O/In ratio of ~ 1.26 ¹⁶. The oxygen vacancies in the film predominantly determine the film resistivity.

Table 3. Effect of film thickness and oxygen concentration during deposition on the resistivity of thin film In_2O_3

Film Thickness (nm)	O_2 in process gas (%concentration)	Resistivity ($\Omega\text{-cm}$)
40	0	0.1
150	0	0.005
260	0	0.009
310	0	0.009
150	10	10
150	25	30
100	25	35

On analysis of these thin films using AFM and stereological techniques, we found that 40 nm films were very smooth with grain size features on the order of 5 nm ($R_{\text{rms}} = 0.3$ nm). As the film thickness increased, the grain size features and roughness also increased (150 nm film = 35 nm; $R_{\text{rms}} = 1.4$ nm and 265 nm film = 58 nm; $R_{\text{rms}} = 4.5$ nm). The sensor response to 5 to 50 ppm NO_x decreased for these films with increasing film thickness from $S \sim 25$ (40 nm films) to $S \sim 2$ (300 nm films). Thinner films had smaller grain size compared to thicker films confirmed by AFM scans. Similar effect of grain size response variation due to film thickness has been observed in literature with other metal oxide films¹⁷⁻¹⁹. Results were consistent with Yamazoe's theory regarding the effect of grain boundaries on sensor response for SnO_2 films when grain/crystallite sizes are comparable to twice the debye length (L_D)¹⁹. The debye length of In_2O_3 was calculated to be approximately 2.4 nm. The carrier concentration for n -type In_2O_3 film from room temperature hall measurements was calculated to be $3 \times 10^{19} \text{ cm}^{-3}$. The particle size for 40 nm thick In_2O_3 film In_2O_3 was 5 nm ($\sim 2L_D$). The 40 nm In_2O_3 film had a $6.5 \times$ higher sensor response when compared to a 150 nm thick film ($S \sim 3$) which had a 35 nm particle size. For particles on the order of $2L_d$ (~ 5 nm), the complete particle will control the charge carrier flow while for bigger grains ($35 \text{ nm} \gg L_d$), the grain boundary contacts influence the charge carrier flow resulting in limited sensitivity as seen for thicker films (~ 300 nm).

Effect of oxygen in sputtering ambient

Increased film thickness resulted in increase in grain size of the In_2O_3 . Deposition conditions also have an important effect on the grain size with samples deposited in 10% O_2 and 25% O_2 affecting gas sensing characteristics as a result of smaller In_2O_3 particles (25 nm and 15 nm) in comparison with samples (150 nm thick) deposited in pure Ar (~ 35 nm) as presented in Fig. 15 (a-b).

Fig. 15. AFM scan ($1 \times 1 \mu\text{m}^2$) on an 8 nm height scale of a (a) 150 nm thick In_2O_3 film (Avg. particle size: 35 nm; $R_{\text{rms}} = 1.4$ nm deposited in pure Ar and (b) a 100 nm thick In_2O_3 film (Avg. particle size: 22 nm; $R_{\text{rms}} = 0.3$ nm deposited in 25% O_2)

Samples deposited in O_2 mixtures generated sensors with high sensor response ($S \sim 50$) as well as a relatively fast response to 25 ppm NO_x at 500 °C as presented in Fig. 16. These results were predominantly attributed to the smaller particle sizes of these thin films. It is believed that sputtering films are compact in nature compared to screen printing and other thick film techniques^{3,8}, whereby the interaction of gases with the In_2O_3 film takes place predominantly at the geometric surface. In_2O_3 thin films deposited in 25% O_2 have more than a 50% reduction in grain size (~ 15 nm) when compared to as-deposited samples (~ 35 nm). The grain sizes for films deposited in 25% O_2 ambient varied from 3 to 20 nm with an average grain size of 15 nm. The resultant increase in grain boundary coverage for O_2 deposited samples as well complete depletion of some of the the grains result in higher sensor response to NO_x .

Fig. 16. Sensor response time constants of In_2O_3 films deposited in Ar, 10% O_2 and 25% O_2 conditions to 25 ppm NO_x operating at 500 °C in ambient N_2 . The responses were fitted with two independent time constants giving the time constants (τ_1 and τ_2) for rise and recovery.

The effect promoter layers on sensor response

In_2O_3 films (~ 150 nm) without promoter layers exhibit slow response ($\tau_{\text{rise}} \sim 63$ seconds) as well as low sensor response to 25 ppm NO_x ($S \sim 5$) at high temperatures (≥ 500 °C). Promoters are materials on a semiconductor surface (In_2O_3) which can help improve the sensing characteristics¹¹. Fig. 17 (a-b) presents the sensor response of 150 nm thick In_2O_3 films as a function of the promoter layers applied including Au promoter and TiO_x promoter to 25 ppm NO_x in N_2 carrier gas operating at 500 °C. The In_2O_3 films with the Au promoter shows the highest sensor response ($S \sim 32$) to 25 ppm NO_x followed by In_2O_3 films with TiO_x promoter ($S \sim 25$). The In_2O_3 film with Au promoter had a faster response ($\tau_{\text{rise}} \sim 15$ s) to 25 ppm NO_x than TiO_x ($\tau_{\text{rise}} \sim 32$ s) and as-deposited ($\tau_{\text{rise}} \sim 63$ s) samples. It is widely believed that Au is non-reactive when deposited as a continuous layer but when present as nano-scale particles on metal oxide surfaces, its chemistry dramatically changes²⁰ enabling applications in gas sensors²¹. Experimentally, oxygen has been shown to strongly adsorb on gold particles²²⁻²⁴. Bond suggested that ultrafine Au particles supported on oxides become electron deficient by donating electrons to the semiconductor²⁴. The catalytic properties of these Au particles resemble Pt, for which the spillover mechanism has been suggested in detecting H_2S ²⁵, CO ¹¹. NO_x gas sensing with noble metals like Au and Pt has been investigated for carbon tube²⁶ and WO_3 based gas sensors²⁷ resulting in faster response and increased sensitivity. Since the size of the dispersed Au particles are small (~ 10 nm), characterized by AFM and SEM, we believe the NO_x strongly adsorbs on the Au surface and spills over to the In_2O_3 . *In-situ* adsorption studies might help to better understand the effect of Au particles on the adsorption of NO_x species for In_2O_3 films considering either spillover effects can occur or changes can be induced in the metal oxide support layers²⁸.

For TiO_x layers, we have not observed any definitive clustering as seen for Au particles, characterized by AFM and SEM. Therefore we infer, the TiO_x catalyst dominates as a surface state controlling the conductance of the semiconductor and thereby the adsorption processes on the catalyst surface affect the semiconductor support as well. This mechanism has been suggested for Ag_2O and NiO catalysts²⁹ and PdO catalyst on SnO_2 support³⁰.

Fig. 17. Sensor response of (a) as-deposited, TiO_x promoter and Au promoter on In_2O_3 films, and (b) time constants for the rise and recovery from exposure to 25 ppm NO_x for as-deposited, TiO_x promoter and Au promoter in N_2 carrier gas operating at 500 °C.

Fig. 18 presents sensor response and time constants for samples deposited in Ar with 25% O₂ and with Au and TiO_x promoter layers to 25 ppm NO_x from 450 to 650 °C in N₂ carrier gas. In₂O₃ samples with Au promoter have the highest sensor response to 25 ppm NO_x (S ~ 50) in comparison with TiO_x promoter (S ~ 21) at 500 °C as seen in Fig. 18. Samples without promoter layers have comparable response (S ~ 47) to Au promoter layers. Large response time of TiO_x layers suggest low adsorption energy for NO_x to adsorb slowing down the sensor kinetics and generating low sensor response compared to as-deposited and Au promoter samples. At higher temperatures (≥ 600 °C), the similar response for all samples indicate the equilibrium between adsorption and desorption favors lower surface coverage. In₂O₃ samples with Au promoter layers consistently have the fastest response constants to NO_x exposures from 400 to 650 °C when compared to In₂O₃ samples with TiO_x promoter and without promoter layers.

Fig. 18. Time constants - τ_{1rise} and τ_{2rise} for In₂O₃ samples (25% O₂) with Au and TiO_x promoter layers on exposure to 25 ppm NO_x (1200 s) in N₂ from 400 to 650 °C

Selectivity of In₂O₃ thin films towards NO_x at high temperature (≥ 500 °C)

Selectivity, stability and reproducibility in the complex and harsh environments are the predominant challenges for metal-oxide state gas sensors. By their very nature, solid state gas sensors have problems with reproducibility and stability. We have investigated the selectivity, stability and repeatability of In₂O₃ solid state sensor at high operating temperatures (≥ 500 °C) in NO_x, NH₃, H₂ and CO₂ test gases typically found in diesel exhaust. In₂O₃ thin films were subjected to cross-sensitivity tests exposing them to 25 ppm NO_x, 100 ppm NH₃, 5000 ppm H₂ and 1000 ppm CO₂ individually as well as in a mixture with 25 ppm NO_x in N₂ carrier gas. Table 4 shows the sensor response characteristics of In₂O₃ thin film with Au promoter towards these gas mixtures at 500 °C in N₂ carrier gas.

Table 4. Sensor response of 150 nm thick In₂O₃ film with Au promoter layer to individual test gases at 500 °C in N₂ carrier gas.

Target Gas	Concentration (ppm)	Gas Sensor Response (S)	Sensitivity (ppm ⁻¹)
NO _x	25	23	0.92
NH ₃	100	-0.5	-0.005
H ₂	5,000	-1	-0.002
CO ₂	1,000	-0.01	1×10 ⁻⁵

The In₂O₃ thin films seems very selective to 25 ppm NO_x (S ~ 23) in N₂ carrier gas. The sensitivity of the sensors is atleast 20× greater to NO_x than other gases in N₂ background. Selectivity tests in 5% O₂ revealed the sensor is selective to NO_x (S ~ 5) with sensor response 4× greater to NO_x than other test gases (S ~ 1). The reduction in NO_x sensitivity in 5% O₂ background, is due to competition for adsorption of sites between NO_x and O₂ on the In₂O₃ surface. True selectivity test for a film is its ability to detect the target gas when mixed with other gases. The sensor selectivity was measured by exposing the samples to mixtures of NO_x with NH₃, CO₂ and H₂ and the results are presented in Fig. 19. NO_x response particularly when mixed with 100 ppm NH₃, or 5,000 ppm H₂ decreases considerably at operating temperature of 500 °C. A similar decrease in response was also observed between operating temperatures 400 to 650 °C. NO_x response in presence of 1,000 ppm CO₂ changes from S ~ 25 to S ~ 13 at 500 °C. When exposed individually to 1000 ppm CO₂, In₂O₃ showed very little sensor response (S ~ 0.01), hence the reduction in sensitivity in presence of CO₂ was attributed to competition for adsorption sites between NO_x and CO₂. Response to NO_x in presence of 100 ppm NH₃ decreases drastically (from S ~ 25 to S ~ 0.6). Chemically NH₃ is known to reduce NO_x without the presence of oxygen in selective catalytic reduction and hence reduces the sensor response drastically with the byproducts N₂ and H₂O^{31,32}. NO_x response in presence of 5,000 ppm H₂ is dominated by the thin film sensor response to H₂. There are potentially two mechanisms for H₂ to affect NO_x sensor response. 1) H₂ individually has low sensor response to In₂O₃ (S ~ 1.3), but in a gas mixture with NO_x, the higher concentration of H₂ blocks adsorption sites for NO_x. 2) H₂ is known to react thermally with NO₂ resulting in the formation of H₂O and NO³³. FT-IR investigations in our work have revealed the absence of NO_x in the reaction chamber in presence of NH₃ at operating temperatures ≥ 600 °C.

Fig. 19. Sensor response and time constants for a 150 nm thick In₂O₃ film with Au promoter layer to 25 ppm NO_x and mixtures of 25 ppm NO_x with 1000 ppm CO₂, 100 ppm NH₃, or 5000 ppm H₂ at 500 °C in N₂ carrier gas.

The In_2O_3 film ($3 \times 2 \text{ mm}^2$) can be ruled out as the catalyst for the SCR reaction since catalysts for automotive applications require large surface area to act as efficient catalysts. The surface area for the most efficient SCR systems ($\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$) in automobiles is about 5 m^2 ³⁴.

The In_2O_3 sensor sits on a heater chuck made from 316L stainless steel containing approximately 65% iron, 18% chromium, 14% nickel content, others < 3% (Mo, Mn, Si, P, S)^{35,36} and has a puck shape with dimensions of $50 \times 20 \text{ mm}^2$ (diameter $\times$ height) and surface area of 0.9 m^2 . The test chamber was also made of 316L stainless steel but was not as hot as the heater chuck. These metals may also be present in the oxide form in the 316L steel³⁶. Oxides of Fe, Cr and Ni have been used as a low temperature ($\sim 200 \text{ }^\circ\text{C}$) SCR catalyst for the NO_x reduction using NH_3 ³⁷. We believe that the Fe, Cr and Ni content in the heater chuck and test chamber act as SCR catalysts for NO_2 reduction using NH_3 .

Stability of In_2O_3 thin films in exhaust based gases

150 nm In_2O_3 thin films with Au promoter were also subjected to stability and cross sensitivity tests to determine the stability and selectivity of these thin films at operating temperatures $\geq 500 \text{ }^\circ\text{C}$ in N_2 carrier gas as presented in Fig. 20. The sensors were subjected to gas sensor tests with the response and recovery time period of 1200 s. The tests investigated the effect of NH_3 and H_2 on the NO_x sensor response and response constants both during and after the NH_3 and H_2 exposures.

Fig. 20. Stability of In_2O_3 films when exposed to NH_3 and H_2 at $500 \text{ }^\circ\text{C}$ in N_2 carrier gas. NH_3 decreases the sensor response by a factor of 2. H_2 etched the In_2O_3 film leading to decrease in sensor response.

Exposure to 5 to 50 ppm NO_x or 100 ppm NH_3 did not significantly change (< 4%) the baseline resistance of the In_2O_3 sensor ($\sim 840 \text{ }\Omega$). After exposure to 100 ppm NH_3 , the sensor response to 25 ppm NO_x decreases from $S \sim 31$ to $S \sim 16$ but then recovers a significant amount of the original sensor response of $S \sim 27$ after two consecutive NO_x exposures. Table 5 gives the sensor response to 25 ppm NO_x before and after exposure to 100 ppm NH_3 . The response

constants with individual time constants can be described by 2nd order reaction kinetics presented in our earlier work³⁸. Response constants to NO_x are given by $\tau_{1\text{rise}}$ and $\tau_{2\text{rise}}$, while recovery constants are given by $\tau_{1\text{recovery}}$ and $\tau_{2\text{recovery}}$. The sensor required two 25 ppm NO_x exposures before it the time constants recovered to pre-NH₃ exposure characteristics ($\tau_{1\text{rise}} \sim 15$ seconds, $S \sim 30$). Exposure to 100 ppm NH₃ did not result in any significant change in the baseline resistance. In summary, the effect of NH₃ exposure on the In₂O₃ NO_x sensor was almost a factor of 2 decrease in sensor response and almost a factor of 3 increase in the response time constant.

Table 5. Sensor response and response constants for a 150 nm thick In₂O₃ to 25 ppm NO_x before and after exposure to 100 ppm NH₃ at 500 °C in N₂ carrier gas.

Response Characteristic	Before NH ₃ exposure	After NH ₃ exposure		
		First pulse	Second pulse	Third pulse
Sensor Response (S)	31	16	24	28
$\tau_{1\text{response}}$ (s)	15	43	21	16
$\tau_{2\text{response}}$ (s)	130	650	184	145
$\tau_{1\text{recovery}}$ (s)	10	6	7	8
$\tau_{2\text{recovery}}$ (s)	112	125	128	131

The sensor resistance quickly decreases, but then steadily rises with exposure to 1,000 ppm H₂. After the exposure (and a subsequent exposure to NO_x) the baseline resistance increased from 950 Ω to about 1,850 Ω . The NO_x sensor response after the first H₂ exposure resulted in decrease of sensor response from $S \sim 31$ to $S \sim 19$, but the response time constants were similar before and after H₂ exposure ($\tau_{1\text{rise}} \sim 15$ seconds, $\tau_{1\text{recovery}} \sim 10$ seconds). A subsequent exposure to 25 ppm NO_x with 1,000 ppm H₂ further increased the baseline resistance to $\sim 2,900 \Omega$. This resulted in a further decrease in sensor response to $S \sim 15$. The increase in baseline resistance resulted from etching of the In₂O₃ film, and was confirmed by XPS (X-ray photoelectron spectroscopy) quantification of the surface composition on In₂O₃ film. This experiment found a dramatic decrease in In and a dramatic increase in Si concentration from the substrate after exposure to 5,000 ppm H₂ at 500 °C in N₂ carrier gas for a time period of 1200 s, indicating the film was partially removed and the substrate partially exposed. The quantified surface composition measured before and after H₂ exposures is presented in Table 6. In applications which have appreciable amount of hydrogen ($\geq 0.1\%$) at temperatures > 500 °C, it is not viable to use In₂O₃ as a NO_x sensor.

Table 6. Composition of In₂O₃ film before and after being exposed to 5,000 ppm H₂ at 500 °C in N₂ carrier gas for 1200 s.

Element	In ₂ O ₃ as-deposited (at%)	In ₂ O ₃ after H ₂ exposure (at%)
O	52.5	50
In	47.5	6.5
Si	0	43.5

Repeatability of In₂O₃ sensor to NO_x

Gas sensing films need to have repeatable sensing characteristics to the target gas during

continuous operation as well as when operated over a period of time (a few years). Fig. 21(a-b) present the repeatability of thin film In_2O_3 deposited in varied conditions to 25 ppm NO_x in N_2 carrier gas at 500 and 600 °C. The sensors were chosen based on having the highest and fastest sensor response³⁸. The sensors chosen were In_2O_3 films (~ 150 nm) sputter deposited in Ar, 10% O_2 and 25% O_2 . All tested layers had an Au promoter layer (~ 5 nm) on top of the In_2O_3 film. The sensors were exposed to 8 cycles each lasting 1200 s using 25 ppm NO_x . The average sensor response and time constants for all NO_x exposures were calculated. The error bars represent the maximum and minimum variation seen in the NO_x response of In_2O_3 thin film sensors which were tested continuously at 500 and 600 °C to NO_x pulses.

Fig. 21. Repeatability characteristics of In_2O_3 thin film sensor to 25 ppm NO_x in N_2 carrier gas for films deposited in pure Ar (0% O_2), 10% O_2 and 25% O_2 at operating temperatures of (a) 500 °C and (b) 600 °C.

Sensors deposited in pure Ar had the lowest sensor response ($S \sim 26$) of the presented films as seen above in Fig. 21(a-b). The average sensor response (S) is $S \sim 26$ at 500 °C and $S \sim 2.5$ at 600 °C. The overall variation in sensor response was $\sim 11\%$ at both temperatures. The variation in response constants (τ_{response}) was about 40% with an average response time constant (τ_{response}) of ~ 50 seconds and ~ 7 s at 500 and 600 °C respectively. The average recovery time constant (τ_{recovery}) of ~ 17 s at 500 °C was slower compared to ~ 5 s at 600 °C with an overall variation of about 60%.

Sensors deposited in 10% O₂/Ar had an average sensor response of $S \sim 36$ with an overall variation of about 9% at 500 °C in N₂ carrier gas towards 25 ppm NO_x. At 600 °C, the average sensor response was $S \sim 4.4$. The sensor also exhibited quicker response with an average τ_{response} of 14 s and 7 s at 500 and 600 °C, respectively. The overall variation in the response constants (τ_{response}) was ± 3 s or about 35% at 500 °C towards 25 ppm NO_x. The average recovery (τ_{recovery}) time constant was ~ 7 s at 500 and 600 °C, respectively, with overall variation of about 80% (± 3 s).

Sensors deposited in 25% O₂/Ar had an average sensor response of $S \sim 46$ and $S \sim 7$ at 500 and 600 °C, respectively. The overall variation in sensor response was 10% at 500 °C and 5% at 600 °C. These sensors were quickest among In₂O₃ thin film sensors at 500 °C with τ_{response} and τ_{recovery} constants of about 5 s with an overall variation of 40% (± 1 s) in response and 80% (± 2 s) in recovery from 25 ppm NO_x. At 600 °C, the response (τ_{response}) and recovery (τ_{recovery}) time constants to 25 ppm NO_x at 600 °C were < 10 s with overall variation of about 40% and 50%, respectively.

Effect of electrode geometry on the NO_x sensor response

The electrodes used to contact the gas sensitive material also play an important role in the operation of the chemical sensor. They should be mechanically and chemically stable without any interference to the gas sensing mechanism³⁹. Efforts to study the effect of electrode geometry on the gas sensitivity have resulted in promising results. Simulation of the electrode geometry⁴⁰ indicated a nominal increase of sensitivity as a function of electrode spacing when electrodes are placed beneath the sensing films but decreased with spacing when the electrodes are placed on top of the sensing film. The electrode material also plays an important role as a Au electrode was found to present the highest sensitivity to H₂ for SnO₂-Mn₂O₃ films at 450 °C compared to Pt and Pd electrodes⁴¹.

To test the effect of the number of electrode pairs on sensor response, 150 nm thick In₂O₃ films with and without Au promoter were tested to 25 ppm NO_x with different electrode geometries (single, two and five pair) at 500 °C. These films had a constant IDE spacing of 300 μm . Multiple tests were conducted to verify the effect of electrode pairs on the sensor response and the results are presented in Fig. 22. Single electrode pair sensors had the highest average sensor response to 25 ppm NO_x for In₂O₃ films with Au promoter ($S \sim 17$) and no promoter films ($S \sim 10$). Multiple IDE pairs (five) had a much lower average sensor response ($S \sim 3$) when compared to an average single electrode pair ($S \sim 17$) with Au promoter layers. For In₂O₃ films with both Au and no promoter layers, we see a similar trend with the number of electrode pairs with Au promoter layer having a higher sensor response ($S_{\text{single}} > S_{\text{two}} > S_{\text{five}}$).

It is also important to note that the In₂O₃ films tested above had low resistivity (0.005 $\Omega\cdot\text{cm}$) compared to other metal oxide films used for gas sensors (TiWO_x, SnO₂, NiO, WO₃ > 0.05 $\Omega\cdot\text{cm}$). The effect based on the number of finger pairs with the same IDE spacing has not been

reported previously for other metal-oxide films mentioned above. This effect was also observed in highly resistive ($1\ \Omega\cdot\text{cm}$) In_2O_3 films where we notice a similar trend with single electrode pair sensors having a $\sim 3\times$ higher sensor response ($S \sim 70$) compared to multiple (five) electrode sensors ($S \sim 24$) and two electrode pair sensors ($S \sim 39$).

Fig. 22. Effect of number of electrode finger pairs on the 25 ppm NO_x sensor response at 500 °C for In_2O_3 sensor with 300 μm electrode spacing.

Effect of system resistance on the baseline resistance was investigated since the In_2O_3 baseline resistance for multiple IDE was on the order of $\sim 40\ \Omega$. The system resistance was experimentally found not to exceed $10\ \Omega$. The system resistance was mathematically subtracted from the overall carrier/test gas resistance and the sensor response was re-calculated. No effect of the baseline resistance was found on the variation of NO_x sensor response as a function of electrode pairs. Four point probe measurements were also performed to discount the effect of external resistance on the NO_x sensor response. Four probe and two probe measurements present similar NO_x sensitivity as a function of number of electrode pairs for In_2O_3 films with Au promoter at 500 °C. The sensor response for In_2O_3 films for single and eleven electrode pairs are of the same order, $S \sim 3$ and $S \sim 28$ for both two probe and four probe measurements. The baseline resistance for four probe measurements was about 20% lower than two probe measurements as expected due to absence of external resistances (probe needles, wires etc.). We can conclude that system resistances do not play a significant part in the variation of gas sensitivity due to electrode geometry.

Investigation of operating temperature (300 to 600 °C) did not reveal any effect on the NO_x sensitivity as a function of electrode geometry. Reports in literature have also suggested non-linearity in I-V measurements when the sensors are exposed to target gases⁴². It is well known that changes in electric field density can affect the adsorption kinetics changing the gas sensitivity⁴³. Resistance is measured by the Keithley 2000 DMM by sourcing a constant current and measuring the voltage. The voltage typically measured is on the order of a few millivolts. I-V measurements were taken using a HP 4145 semiconductor parametric analyzer. The voltage was swept from -20 to +20 VDC and compliance was set at 0.1 A. Fig. 23 presents the I-V

measurements for single and five electrode pairs to 25 ppm NO_x sensor response for In₂O₃ sensors without promoter layers and with Au promoter layers.

Fig. 23. I-V measurements for In₂O₃ sensors exposed to 25 ppm NO_x at 500 °C in N₂ carrier gas for a) single electrode pair b) five electrode pairs c) single electrode pair with Au promoter and d) five electrode pairs with Au promoter.

In₂O₃ sensors with single and five electrode pair sensors have a linear response at 500 °C in N₂ carrier gas as presented in Fig. 23 (a-d). The linear measurements in N₂ carrier gas discount the interference of electronic valves, measurement systems, heater electronics on the sensor response of In₂O₃ films. Exposure to 25 ppm NO_x for multi-electrodes does not result in any significant non-linearity especially in the -5 to +5 VDC range as presented in Fig. 23 (b, d) for five pair electrode sensors which present a reduced sensor response. The operating voltages measured for the sensor during operation are less than < 1 VDC. For single-electrode pair sensors with Au promoter layers, there is significant non-linearity > 5 VDC for presented in Fig. 23 (c). Overall, we do not see significant non-linearity in the I-V measurements near the operating voltage (< 1 VDC) suggesting the strong reduction in sensor response is not due to

applied electric field affecting the gas adsorption characteristics.

The change in sensor response as a function of electrode pairs for In_2O_3 thin films was observed for both Au and Pt electrodes. It may be possible that we may be observing catalytic effects of the noble metal electrode with In_2O_3 thin films. Gas sensitive tests with NiO thin films towards H_2 and TiWO_x thin films towards NO_x as a function of number of electrode pairs have revealed absence of variation in gas sensitivity. *In-situ* adsorption/catalytic studies at the electrode-metal oxide interface can reveal possible causes for changes in the gas sensitivity.

Part III: Ga_2O_3 thin films

Gallium oxide films were investigated as a potential CO_2 gas sensor material. Ga_2O_3 has a high melting point and low vapor pressure, and therefore has the reasonable expectation of being stable at high temperatures. There is very little literature regarding CO_2 sensing properties of metal oxide semiconducting gas sensor materials. This is the results of the very inert character of CO_2 , which evidence suggests does not easily chemisorb onto surfaces, and therefore has lower chances of participating in the traditional MOX gas sensing mechanism. Indeed, the gas sensor response of Ga_2O_3 to CO_2 test gases were quite small for concentrations up to 2,000 ppm. We also investigated their response to H_2 test gases, and did find significantly higher responses for this gas. H_2 was also found to etch the films, as was also the case for In_2O_3 films. Based on the dramatically better sensor responses achieved for NiO films that have been previously reported, we focused more NiO and In_2O_3 films for this project.

Gallium oxide is a is an *n*-type semiconductor, all the layers were deposited via RF sputtering using the Perkin Elmer 4400 Production Sputtering System. This system offers the possibility of both DC and RF sputtering. It is equipped with a load lock and the main chamber in which three 200 mm targets are mounted. A stepper motor that was additionally installed in the system allows the wafer chuck to oscillate underneath the target in order to achieve a better layer homogeneity. Deposition was usually started after the main chamber had reached a pressure of less than 3×10^{-6} Torr. The parameters that mainly influence the layer thickness and characteristics are sputtering time and the applied power and gas pressure. Sputtering pressures between 10 mTorr and 40 mTorr were used and the power varied from 100 to 500 W. In order to assure a reliable reproducibility of the layers, sputtering rates were determined for different deposition parameters. Thereto, a SiO_2 witness sample was used for every sputtering run beside the test structures and their thicknesses were measured via ellipsometry and by means of a profilometer. The sputtering rate was calculated from the quotient of layer thickness and deposition time. The measuring principle of a profilometer consists in scanning the surface and detecting thickness variations. For that purpose an edge has to be created on the sample to obtain a step that can be measured. This was realized by drawing a line with an overhead marker on the witness sample before deposition. Later the line with the sputtered gallium oxide on top was washed away by putting the sample for some seconds into an acetone bath. For estimating the thickness via ellipsometry the refractive index of gallium oxide has to be known approximately (1.80 - 1.91). By means of analysis models the layer thickness can be calculated if optical properties (refractive index) are known.

Table 7. Thicknesses and deposition rates for samples deposited using different parameters.

Sample #	24	20	9	21	11	6	8
Power [W]	300	300	300	300	100	400	500
Pressure [mTorr]	10	20	30	40	30	30	30
Time [min]	12	20	35	13	50	20	10
Thickness (Profilometer) [nm]	120	180	279	78	120	198	128
Thickness (Ellipsometer) [nm]	120	172	277	88	126	206	124
Thickness (Average) [nm]	120	176	278	83	123	202	126
Deposition rate [nm/min]	10.00	8.80	7.94	6.38	2.46	10.10	12.60

The structure of all films were investigated via X-ray diffraction (XRD). This is a standard laboratory method for gaining information about lattice parameters, grain size and strain of a crystalline material. For the gallium oxide layers, XRD was primarily used for determining the crystal structure. Fig. 24 shows XRD results for an as-deposited layer and for the same layer that was annealed under different conditions. It is observable that the as-deposited layer is amorphous as no peaks appear. The narrow peak at approximately $2\theta=33.1$ is typically to be assigned to silicon. This (002) peak is only visible due to stress and does not occur for all samples. The spectra of gallium oxide films that were annealed in nitrogen or in the nitrogen-oxygen mixture feature some other peaks. These are consistent with the peak positions for monoclinic gallium oxide. The peak intensities do not necessarily have to match the reference intensities, neither are all typical peaks expected to appear because the investigated layer is very thin (85 nm). Thicker layers (>120 nm) exhibited more intense reflections. There is no other known gallium oxide structure that corresponds to the measured structure. No significant differences were observed from samples annealed in N_2 or synthetic air. The XRD curves are all similar, and the full-width at half maximum (FWHM) values of the peaks do not differ significantly. The smaller the FWHM values of the peaks are, the higher is the crystallinity of the investigated sample. That means the crystallization does not change any more after 5 h annealing. There is neither a difference observable between 900 and 1000 °C nor between nitrogen and nitrogen-oxygen ambient.

As the conducting mechanism of gallium oxide relies on oxygen vacancies to generate charge carriers, pure nitrogen was chosen as standard annealing gas. Oxygen can react with the sample and cause a decrease in the charge carrier concentration. Concerning the sample annealed in forming gas (98% Ar: 2% H_2), the Ga_2O_3 film was etched away, which is consistent with the etch of In_2O_3 films in H_2 containing ambients. The XRD diagram does not show any typical gallium oxide peaks either. Though there appears one small peak at around $2\theta=28$, it is not clear to which material it refers. Gallium oxide has obviously reacted with the ambient gas likely H_2 , as formation of Group III hydrides is known from chemical vapor deposition (CVD), and was also observed for In_2O_3 films. For these reasons, a 5 h annealing process at 1000 °C in nitrogen was used for the following samples.

Fig. 24. XRD spectra for an unannealed sample and the same sample annealed under different conditions. The sample was deposited at 500 W and 30 mTorr, and has a thickness of 85 nm.

In Fig. 25 XRD curves of samples deposited at different pressures are pictured. For all three samples a deposition power of 500 W was applied. Thus, the deposition pressure is the only variable that can affect the crystallinity of the sample. Peak heights do not provide information about crystallinity as they depend on the layer thickness. A very small incline of the sample during XRD measurements can also lead to an observable change in peak heights. However the FWHM values of the peaks are a better measure for the crystallinity. The lower the FWHM values are, the higher is the crystallinity. Table 8 shows the peak positions and FWHM values of the XRD measurements mapped in Fig. 25. It is noticeable that samples deposited at lower pressures tend to exhibit lower FWHM values. The three samples possessed the same FWHM value for the silicon peak at 69.3°. This is a good precondition for achieving reasonable results by comparing the gallium oxide peaks. It is gathered from that that crystallinity can be enhanced by applying lower deposition pressures.

Fig. 25. XRD spectra from Ga₂O₃ films collected as a function of deposition pressure for Ar pressures from 10 to 30 mTorr.

Table 8. XRD peak positions and FWHM values for annealed samples deposited at different pressures.

Nr 13-3 (30 mTorr)		Nr 25-1 (20 mTorr)		Nr 25-1 (10 mTorr)	
Peak Pos. [°2θ]	Fwhm [°2θ]	Peak Pos. [°2θ]	Fwhm [°2θ]	Peak Pos. [°2θ]	Fwhm [°2θ]
18,977	0,945	19,021	0,787	19,069	0,630
30,310	0,394	30,265	0,551	30,309	0,551
-	-	33,087	0,157	33,101	0,098
38,412	0,945	38,591	0,236	38,586	0,276
-	-	59,667	0,945	59,442	0,787
-	-	68,915	0,12	68,918	0,072

Surface morphology of gallium oxide layers was further investigated using atomic force microscopy (AFM). AFM was applied for different gallium oxide films before and after annealing. Fig. 26 (a-b) show AFM pictures of a 273 nm as-deposited sample and the same sample after annealing at 1000 °C in nitrogen for 5 h. The surface morphology has changed suggesting changes in the film microstructure likely related to crystallization or crystal growth. The most significant parameter for the actual roughness of a film is the Root mean square value (RMS) of roughness (R_{RMS}). Generally, it only makes sense to compare layers that hold approximately the same thickness. Fig. 26 (c-d) draw such a comparison of the surfaces of samples fabricated at different deposition pressures. Again, all samples were annealed in nitrogen for 5 h at 1000 °C. Clearly lower sputtering pressures provoke higher grain growth. An eye-catching characteristic is the annular arrangement in some areas. Surface roughness

increases with increasing deposition pressure. The deposition power does not feature such a wide influence on the surface morphology. However, a small increase in roughness is recorded for higher powers, but the impact is very small and could also occur because of normal variations around the mean roughness value. All layers hold thicknesses between 120 nm and 130 nm, i.e. the thickness differences are small. Therefore, the impact of the thickness differences on the surface roughness can be neglected.

Fig. 26. AFM micrographs taken as a function of deposition and annealing conditions for Ga_2O_3 thin films including (a) a 273 nm film deposited at 30 mTorr and 500 W and (b) after annealing in N_2 for 5 h at 900 °C. Also, representative micrographs from films deposited at (c) 10 mTorr and 500 W, and (d) 20 mTorr and 400 W are also presented.

X-ray photoelectron spectroscopy (XPS) was used to measure the composition of gallium oxide (Ga_2O_3) layers, as these films were much less than 1 μm in thickness, and therefore could not be easily measured by SEM/EDX techniques. Gallium oxide layers were analyzed untreated and after a 240 s ion beam etching process to remove contaminants from the surface. The results for two different samples are listed in Table 9. Gallium and oxygen are the main constituents, and there is only a small amount of carbon which observed on all surfaces exposed to the

atmosphere. Only the major peaks are listed as they allow sufficiently accurate conclusions about layer composition.

The most interesting values are the atomic concentrations of the detected elements. As the chemical formula of gallium oxide is Ga_2O_3 a ratio of two parts gallium to three parts oxygen is expected which would accord with 40% gallium and 60% oxygen. The untreated samples exhibit slightly differing values, especially less gallium oxide than expected, but up to 10% carbon. Hence, a 240 s ion beam etching was applied in both cases. After the removal of contaminations, the newly measured atomic concentrations offer a more reliable predication of the actual material composition. There is only very few carbon remaining (0% and 0.16%, respectively), that is the layer consists of nearly pure gallium oxide. The fact that the atomic concentration of gallium is higher and the one of oxygen lower than supposed by the chemical composition is highly desirable with regard to the conduction mechanism. It is important to attain a perceptible amount of oxygen vacancies as they serve as *n*-type dopants. These films are considered to be stoichiometric within the accuracy of quantification by XPS. In addition, the high resistance of these films at room temperature (reported below) suggest that the concentration of electrically active native defects (intrinsic dopants) is low.

Table 9. Composition of Ga_2O_3 films measured by XPS as-received, and after 240 s of Ar ion etching to remove surface contamination.

Sample # 2: Deposited at 30 mTorr, 500 W						
Untreated						
Peak	Position BE [eV]	Fwhm [eV]	Raw Area [CPS]	Atomic mass	Atomic Conc. [%]	Mass Conc. [%]
Ga 2p	1120.050	1.610	54825.0	69.725	27.62	63.28
O 1s	532.750	1.673	16471.4	15.999	62.27	32.73
C 1s	286.500	1.237	975.2	12.011	10.11	3.99
After 240 s Ion Beam Etching						
Ga 2p	1119.750	1.663	96573.0	69.725	43.99	77.39
O 1s	532.550	1.524	16390.2	15.999	56.01	22.61
C 1s	288.000	0.105	0.0	12.011	0.00	0.00

The custom built gas sensor test station employed for all the gas sensor tests during this project was used to measure the gas sensing properties of the Ga_2O_3 films. The sensor that is to be investigated is placed on a chuck consisting of stainless steel. Watlow cartridge heaters allow a heating-up of the chuck to temperatures up to 650 °C. Therefore, it was not necessary to use the heater that is integrated in the test structure. The contact pads of the finger structures of the chip are connected via probe needles with a Keithley digital multimeter. By applying a current on the needles, the voltage between the finger structures and the resistance is captured by the multimeter. A computer that is interconnected to the multimeter displays the detected resistance versus time. Resistances below 100 MΩ can be recorded. The test gas is usually diluted in carrier gas in order to adjust a certain test gas concentration.

Similarly as for annealing, nitrogen was chosen as standard carrier gas, since it is relatively inert. The fact that changing the mass flow of nitrogen did not affect the resistance of gallium oxide suggests that nitrogen does not react with the sensitive layer. Only a very small temperature-induced decrease or increase of the resistance was observable when the nitrogen flow was changed. The conductance of gallium oxide strongly depends on the applied temperature. Hence, it was generally waited until the sample had reached exactly the adjusted temperature to avoid temperature-induced changes in the resistance during gas tests. At room temperature no resistance can be measured by the multimeter as it exceeds the possible measuring range due to the wide band gap of gallium oxide. Above 250 °C resistance is low enough to be detected with the test structures that possess the closest finger spaces. With the second closest finger spaces, recording data starts between 300 and 400 °C and for the wide spaces there is mostly no resistance value ascertainable. As the resistance of air is in the high MΩ range, it is vital to obtain resistance values in the kΩ range for gallium oxide in the operating mode. This assures that exclusively the conductance of the sensitive layer is recorded. Therefore, only the closest and second closest finger structures were used, as experiments point out that for wider finger spaces the resistance is in the 10 to 100 MΩ range.

As a result, new sensitive layers were produced using deposition pressures of 20 mTorr and 10 mTorr, powers between 300 and 500 W, and by means of the determined deposition rates all samples had thicknesses between 120 and 130 nm. As a verification of the previous assumptions, all of these sensors turned out to be sensitive against 1111 ppm hydrogen. Tests were also performed with 2000 ppm carbon dioxide and sensitivities were observable, indeed lower sensitivities than to 1111 ppm hydrogen. Enhancing the entire gas flow leads to a cool down that causes a resistance change. Anyway, the impact of carbon dioxide on the resistance of gallium oxide exceeds by far the changes that were observable by changing the mass flow of nitrogen. Therefore, the temperature change, induced by a mass flow change, is ruled out as a cause for the resistance change. Carbon dioxide holds an oxidizing impact on gallium oxide. The resistance increases during exposure. Representative data is presented in Fig. 27 for (a) H₂ and (b) CO₂, respectively, at an operating temperature of 500 °C. The films were etched when exposed to H₂ at operating temperatures of 600 °C.

Fig. 27. Gas sensor response measurements taken from Ga₂O₃ films operating at 500 °C to (a) 1,111 ppm H₂, and (b) 2,000 ppm CO₂.

Conclusions

Gallium oxide sensors were produced that are sensitive to different gases at high temperatures $> 500\text{ }^{\circ}\text{C}$. For that purpose, gallium oxide thin films were deposited using the sputtering technique and annealed under different conditions. XRD results revealed that as-deposited gallium oxide holds an amorphous structure and passes into a polycrystalline structure after annealing. As this monoclinic structure is the only stable phase of gallium oxide, this suggests no phase changes will occur with heat treatments or during high temperature operations. The optimized annealing conditions were found to be in nitrogen atmosphere for five hours at $1000\text{ }^{\circ}\text{C}$. Surface morphology was investigated via AFM. Crystal growth after annealing was observable, and it was proven that higher surface roughnesses occur for layers that were deposited at higher pressures and higher grain growth for samples deposited at lower pressures. In order to determine the layer composition, XPS was applied for different samples. It was assessed that the films consist of little more than 40% of gallium and little less than 60% of oxygen which is exactly the desired composition to ensure a certain amount of oxygen vacancies in the material. Gas sensitivity of gallium oxide was tested against hydrogen and carbon dioxide at $500\text{ }^{\circ}\text{C}$. Thereby responses to 1111 ppm hydrogen of up to 0.96 were achieved and up to 0.7 during exposure to 2000 ppm carbon dioxide. Note that significant responses were achieved for detecting H_2 , but these responses appear smaller because the sensor resistance decreased instead of increased, which leads to an inherently smaller range of values based on how the gas sensor response is calculated.

For the gas sensing films tested, at $500\text{ }^{\circ}\text{C}$, it was ascertained that the optimal film thickness is 120 nm. Furthermore, films deposited at low pressures point out a better gas sensing behavior. While 30 mTorr is too high, the sensors fabricated at 20 mTorr deposition pressure feature the best sensitivities and those deposited at 10 mTorr the best time constants.

II. B. Electrochemical Ceramic Materials

Description/Rationale

This section of the project investigated new electrochemical ceramics materials as gas sensitive layers for temperatures $> 500\text{ }^{\circ}\text{C}$. Electrochemical ceramics have been used in gas sensors due to their high selectivity and reliable sensitivity often at very high temperatures. Work this quarter focused on $\text{BaZr}_{1-x}\text{Y}_x\text{O}_{(3-x/2)}$, which is known to be sensitive to water vapor at elevated temperatures, however the material has not been studied for use as a sensor in thin film form.

Results and Discussion

BaZrO₃ Thin Films

The main objective of this work was to develop, fabricate and investigate Y-doped BaZrO_3 thin films for the use in microfabricated high temperature ($T \geq 500\text{ }^{\circ}\text{C}$) humidity sensors. This material becomes conductive at high temperatures, typically above $500\text{ }^{\circ}\text{C}$, with its conductivity depending on temperature, water vapor, and other gas concentrations. These characteristics open up a wide range of existing and potential new applications in industrial process control, energy, and automotive applications. Using microfabrication may lead to comparably cheap, mass produced devices with very small dimensions. The use of thin film technology may also enable faster sensor response times. Literature reports on these materials have focused primarily on bulk

or thick film material prepared by ceramic techniques of a few microns to several millimeters thickness. The present work has studied Y-doped BaZrO₃ thin films of 30 to 750 nm thickness fabricated into sensors for measuring of relative humidity at high temperatures ($T \geq 400^\circ\text{C}$).

In order to accurately measure a large variety of gaseous species and concentrations, the reliable measurement of water vapor is essential since the water vapor can have a huge impact on the accuracy of other gas measurements at high temperature. Many examples of humidity sensors based on chemisorption (surface adsorption) of H₂O or water vapor have been reported^{44,45}, but often 1) lack selectivity towards NO_x, and O₂ at high temperature⁴⁶⁻⁴⁹, and 2) exist only in bulk material or thick film forms^{50,51}. To be suitable for high temperature humidity sensors, the materials must have suitable conductivity (*i.e.*, neither too low nor too high) and high selectivity towards H₂O. Perovskite oxides are particularly attractive for high temperature applications because of: 1) high melting and decomposition temperatures, 2) microstructure and morphology stability, improving the reliability and long-term sensor performance at high temperatures, and 3) an atomic structure with two differently sized cations that are suitable for a variety of dopants and that allow the control of the electrical transport and catalytic properties of the material to optimize sensor performance for specific applications. Y-doped BaZrO₃ combines not only high proton conductivity with excellent mechanical strength, but also have chemical stability under CO₂-containing atmospheres, which is highly relevant for combustion monitoring applications. Wang and Virkar investigated the electrical conductivity at various partial pressures oxygen and water in the temperature range of 500 to 800 °C of 7 wt% Y-doped BaZrO₃ bulk material (10 ~ 100 mS/cm) and have demonstrated high selectivity to humidity during gas sensor tests. Therefore, Y-doped BaZrO₃ is a promising sensing material for high temperature humidity microsensors allowing for 1) high melting temperature ~ 2600 °C⁵², 2) high conductivity (10 μS/cm ~ 10 mS/cm)^{50,52-58}, 3) excellent mechanical strength up to 86 MPa⁵⁹, and 4) high chemical stability in humid and CO₂-containing atmospheres⁵⁰.

Film Deposition and Properties

Major effort went into developing the process parameters for deposition and the characterization of these thin films. Y-doped BaZrO₃ thin films with thicknesses of between 200 and 750 nm were sputtered onto oxidized 50 mm *n*-type Si wafers at room temperature from a ceramic target in an Ar sputtering ambient. Various deposition pressures (0.45 to 50 mTorr) and deposition powers (50 to 300 W) were used in order to understand the correlation between process parameters and film properties. Films were annealed at 800 and 1000 °C for 3 hours in air. The resulting films were characterized using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Atomic force microscopy (AFM) to determine their film compositions, microstructure, and surface morphology. Samples deposited by pulsed-laser deposition (PLD) (30 to 500 nm) were deposited onto identical substrates at substrate temperatures from room temperature to 800 °C in a VAC PLD system. All PLD samples were characterized as deposited. Selected PLD samples were also annealed at 1000 °C for 3 hours in air and characterized again. Transmission electron microscopy (TEM) was used to confirm the particle sizes of 30 and 50 nm PLD films with AFM technique.

Annealing processes are generally used to cause microstructure changes in the material, which may yield more stable and reproducible sensor measurements at high temperatures. In our samples, mud flat cracking was observed in more than 60% of sputtered samples and in all annealed PLD samples, indicating potentially high tensile stress. Stress data for sputtered films were determined based on measurements of changes in wafer/sample bow with a Tencor stylus

profilometer before and after annealing (Fig. 28) and using the following equation

$$\sigma_{stress} = \frac{1}{6} \left(\frac{1}{R_{post}} - \frac{1}{R_{pre}} \right) \frac{E}{(1-\nu)} \frac{t_s^2}{t_f}, \quad (3)$$

where σ_{stress} is stress in the film after the deposition ($[\sigma_{stress}] = 1 \text{ MPa}$), R_{pre} is the substrate radius of curvature before deposition, R_{post} is substrate radius of curvature after deposition, E is Young's modulus ($[E] = 129 \text{ GPa}$), ν is Possion's ratio of substrate ($[\nu] = 0.28$), t_s is substrate thickness ($[t_s] = 1 \mu\text{m}$), and t_f is film thickness ($[t_f] = 1 \mu\text{m}$). Film stress was not determined for PLD samples due to the small substrate size, which renders the determination of the stress using changes in wafer or sample bow too inaccurate to allow comparison with data generated with larger samples.

Fig. 28. Film stress as a function of deposition pressure for RF sputtering samples at deposition pressure between 0.45 and 2.5 mTorr.

Based on the result, while the overall range of stress observed cover compressive and tensile stresses from -80 to +110 MPa, the majority of sputtered samples exhibits tensile stress. Some samples appear to very low stress ($\pm 10 \text{ MPa}$). This drop in stress may be caused by the cracking of the films allowing for a partial relaxation of the film.

The chemical composition of the films was measured by XPS from as received samples, and after 4 minutes ion beam etching. The film compositions were quantified from the spectra. The Ba atomic concentration in the films was studied and compared as shown in Fig. 29 (a-b).

Fig. 29. Ba atomic concentration (AT%) quantified by XPS measurements after 4 minutes ion beam etching for (a) sputter deposited samples as a function of deposition pressure between 0.45 and 2.5 mTorr. Ba AT% ranges between 2% and 18%, showing a *dramatic* Ba deficit compared to the 20% desired Ba content. Also for (b) PLD deposited samples as a function of substrate temperature during deposition.

We identified *dramatic* Ba deficiencies in all deposited layers for both deposition methods. The sputtering deposition appeared to have smaller process windows for closer stoichiometric compositions of 20 wt% Y- doped BaZrO₃ thin films. The much more significant Ba deficiency in the sputtered samples likely results from a re-sputtering affect and may also be the reason for the cracking of the films. The PLD film compositions are closer to the nominal target composition with stable Ba content at all substrate temperatures. The results suggest that

sputtering has a smaller process window for fabricating controlled stoichiometry of Y-doped BaZrO₃ thin films compared to PLD.

XRD spectra were collected to investigate the microstructure of the sputtered and PLD films, and are presented in Fig. 30. The reflections indicate that as deposited sputtered films were amorphous and became polycrystalline after heat treatment. As deposited PLD samples with substrate temperature of 800 °C were polycrystalline in character. The dashed vertical lines on the plots represent the JCPDS values for (110), (111), (200), (211), (220), and (321) reflections for BaZrO₃. The reflections are shifted to higher 2θ values compared to the JCPDS database, which would be consistent with the films being under compressive stress in the out-of-plane direction. These results are also consistent with the presence of the (200) Si peak, a normally unallowed peak, which appears due to strain in the Si substrate. Another possible reason for the shift of the reflections is the Ba deficiency as indicated in Fig. 29. The reflection heights of BZO (110) and BZO (211) reflections were increased with increasing film thickness for both sputtered and PLD deposition (Fig. 31(a)). The reflections also show that PLD samples have a more pronounced reflection than sputtered samples in all cases. The FWHM value appears to decrease with increasing film thickness for both sputtered and PLD films (Fig. 31(b)). This is consistent with both a thinner film and a decrease in crystal quality of the film, which could be caused by damage in the crystal, e.g. expanding of grain sizes.

Fig. 30. XRD reflections collected from as-deposited and annealed sputtered samples and as deposited PLD and annealed samples.

Fig. 31. (a) XRD reflection height versus film thickness for Y-doped BaZrO₃ sputtered films and PLD samples, (b) Full width at half maximum (FWHM) versus film thickness for Y-doped BaZrO₃ sputtered films and PLD samples, with film thickness from 30 to 750 nm.

AFM was used to characterize the surface morphology of as deposited PLD films. AFM micrographs for both samples have a similar surface morphology consisting of nano-scale surface particles. For each film thickness, 6 individual measurements were made using stereological techniques. The results in Fig. 32 show that RMS roughness increased from 1.3 to 4.2 nm and particle size increased from 70 to 170 nm with film thickness from 200 to 500 nm for sputtered films. And particle size (19 to 72 nm) was observed for PLD films and also increased with increasing film thickness. RMS roughness of PLD samples was approximately 4.25 Å.

Fig. 32. RMS roughness and particle size versus film thickness for Y-doped BaZrO₃ for sputtered and PLD films.

TEM data were collected to confirm the particle size of Y-doped BaZrO₃ thin films. Fig. 33 presents TEM images of a) 30 nm and b) 50 nm PLD films deposited at a substrate temperature of 800 °C in vacuum.

Fig. 33. TEM images for PLD films at substrate temperature of 800 °C in vacuum with thickness of (a) 30 nm and (b) 50 nm.

TEM data indicates a particle size of between 17 nm and 25 nm for 30 nm films, and between 20 nm and 26 nm for 50 nm films. This constitutes a difference of 4% to 9% compared to the AFM measurements and confirms that the stereological technique gives a reasonable approximation of the particle size.

Overall, 212 different combinations of sensor devices were made. The first 25 sensor devices using sputtered films had the sensing material deposited on top of the interdigitated test structure (IDE) and showed no response to humidity. The rest of the sensors were fabricated with the IDE on top of the sensitive material, yielding varying degrees of gas sensor response. Another 25 sensors with sputtered films used Ti/Pt as metal contacts for humidity measurements, resulting in unstable and/or unrepeatable humidity response. The 50 remaining sensor devices using sputtered films as well as the 12 PLD sensor devices used Cr/Au as IDE (Fig. 34) on top and produced fast, sensitive, selective, and long term stable humidity response. Therefore, Cr/Au IDE metallization deposited on top of the sensing film yielded the most repeatable and stable humidity sensor responses, but does limit the operating temperature to $< 1000\text{ }^{\circ}\text{C}$ due to the melting point of Au.

Fig. 34. (a) 2D design of interdigitated electrodes (IDE) test structures, with resistive temperature device (RTD), interdigitated electrodes (IDE), heater, and sensitive layer; (b) fabricated test structure.

The sensor conductivity as function of temperature was characterized from 200 to 650 $^{\circ}\text{C}$ to determine the variation of base line resistance with temperature during humidity measurements and to gain information on potential electrical conduction mechanisms in the material.

The conductivity of the samples increases exponentially with increasing temperature (Fig. 9). This relation can be described as [14-15]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (4)$$

where σ is the conductivity as function of temperature in S/cm, σ_0 is the conductivity at 473 K (i.e. the lowest temperature at which we were able to get measurable conductivity values) in

S/cm, E_a is the activation energy in eV, and k is Boltzmann's constant (8.617×10^{-5} eV/K). The activation energy was calculated based on approximate linear fits in the log-plot of film conductivity versus temperature (200 to 650 °C) in N_2 ambient gas at a flow of 1,380 sccm. Using a linear approximation for the slope, two distinct temperature regions can be identified with different slope. This change in activation energy can be interpreted as a change in electrical conduction mechanism. Two distinct regions of activation energies were apparent in the electrical conductivity measurements, consistent with our expectations that electrons and electron-holes were the primary charge carriers at lower temperature ($T \leq 500$ °C), and oxygen ions were the primary charge carriers at high temperature ($T \leq 650$ °C) prior to exposure to water vapor at high temperature. The activation energies seemed to increase with increasing film thickness in both temperature regions. The resulting activation energies for the sputtered samples were only slightly larger than PLD samples at lower temperatures (200 to 500 °C) and much larger at higher temperature (500 to 650 °C) (Fig. 35).

Fig. 35. Activation energy (E_a) versus film thickness for both annealed sputtered samples with film thickness from 200 to 500 nm, and as deposited PLD films with film thickness from 30 to 500 nm.

All samples are initially exposed to dry N_2 gas. Then, water vapor is introduced into the test chamber. Once the electrical conductivity has stabilized, the atmosphere is changed back to dry air. Film sensitivity as stated below is calculated based on:

$$S = \frac{(\sigma_g - \sigma_0)}{(\sigma_0 \times \Delta C)} \quad (5)$$

where S is the sensitivity in atm^{-1} , σ_g is the conductivity upon exposure to humidity at a given temperature T , σ_0 is the initial conductivity without humidity exposure at the same temperature. ΔC is the change in partial pressure of water in atmosphere. Sensitivities up to 65 atm^{-1} for sputtered sample at 400 °C were measured. Most PLD samples have a order of magnitude less humidity sensitivity than sputtered samples, however, PLD samples operates at higher

temperature range. And sensitivity up to 29 and 18 atm^{-1} were measured for PLD samples at 600 and 650 °C (Fig. 36).

Fig. 36. Humidity sensitivity as function of film thickness for sputtered and PLD thin films were tested at water partial pressure of 0.058 atm at temperatures of 400, 500, 600, and 650 °C.

The humidity sensitivity increased with decreasing film thickness for sputtered films in all cases suggests that a surface exchange dominates the conduction. PLD films with exception of 30 and 50 nm films also have the same trend. 30 and 50 nm films have sensitivities that are significantly higher than for thicker samples, also supporting our hypothesis of increasing humidity sensitivity with reducing film thickness. This behavior indicates that more defects which allow absorption of H_2O into the lattice and increase conductivity may exist in the surface layers than in the material bulk. As observed in multiple samples, the humidity sensitivity for 50 nm PLD film is consistently higher than that for 30 nm films, which could potentially indicate a change in trend or mechanism. Reasons for this change could lie in the technical challenges in contacting such a thin layer of sensitive film or in the beginning dominance of scattering effects for charge carriers at the interface between sensitive layer and substrate and at the top surface.

We have characterized and correlated the response times of the sensors and the film thickness at operating temperature. The response time is defined as the time required for the conductivity of the sensor element to reach 60% of the equilibrium value following a step increasing in water vapor concentration. The sensor response time 6 to 27 s were measured for sputtered films and 17 to 56 s were measured for PLD films at partial pressure of water at 0.058 atm. Response time is increasing with increasing film thickness and partial pressure of water, and is increasing with decreasing operating temperature (Fig. 37). Response time (τ_{60}) of sputtered films is faster than other PLD samples. A possible explanation for the faster sensor response could lie in the different surface roughness as showed in AFM measurements or different film density.

Fig. 37. Response time (τ_{60}) for sputtered thin films at temperatures of 400 °C and PLD thin films at 500, 600, and 650 °C. The sensor devices were tested at water partial pressure of 0.058 atm.

In order to test cross sensitivity or selectivity, the sensitive films were exposed to various test gases that would be present in typical high temperature humidity sensing applications. Fig. 38 (a) presents the response of 400 nm thick sputtered Y-doped BaZrO₃ to different test gases at 400 °C, (b) presents the response of 500 nm PLD films to different test gases at 500 °C. N₂ and air were used as carrier gases. NH₃, NO₂, H₂, O₂, CO₂ and humidity were used as test gases.

Fig. 38. Cross sensitivity measurements of Y-doped BaZrO₃ thin films (a) 400 nm sputtered samples at 400 °C and (b) 500 nm PLD samples at 500 °C.

Film produced by both methods showed at least one order of magnitude higher selectivity towards humidity than other gases, which indicating the sensitivity was dominated by humidity. Samples appeared generally stable in mixed gases, some small amount of conductivity changes can caused by the stability of the sensor itself.

Life-time of the sensors is a major factor in evaluating the stability of the films and sensors and thus their relevance for future applications. We stored all humidity samples in gel-pac boxes at room temperature in the Utah Nanofabrication Laboratory clean room upon completion of the initial test runs. The sensors were then retested under identical conditions at regular time intervals. For each test cycle, the sensors were first placed into the test chamber while exposing them to dry N₂ gas at 1380 sccm while ramping up to the operating temperature for 2 hours to stabilize the initial electrical conductivity of the material. Then water vapor was introduced into the test chamber. Once the electrical conductivity values have stabilized, the atmosphere is changed back to dry N₂. We have recently presented long term stability for selected PLD films in excess of 52 weeks. Fig. 39 below illustrates the change in sensitivity and base resistivity of the 200 and 400 nm PLD humidity sensors over a period of 52 weeks with the corresponding film base resistivity as an indicator of sensor stability. Long term stability and life time testing showed that the sensor devices were able to operating functionally in excess of 52 weeks of time, indicating usefulness for real world applications.

Fig. 39. The stability test of the PLD humidity sensors of 200 and 400 nm films during 52 weeks with the corresponding base resistivity at 500°C.

Conclusions

We developed, fabricated and investigated YBZO thin films for the use in high temperature humidity sensors. We focused on the development of process parameters using sputtering and PLD, characterization of the thin films by studied film stress, composition, microstructure, morphology, fabrication on sensor devices with different metal contacts, and also characterization of sensor performances by studied sensor response to humidity, response time, selectivity, and stability of the sensors. We tried to explain possible conduction mechanism by measuring activation energy to compare with literature values. The sensor devices were recorded as being 4 to 20× faster in sensor response (τ_{60}) than other humidity sensor devices (Fig. 40).

Fig. 40. Operating temperature range and time constants for humidity sensors in the market and the research domain, and based on Y-doped BaZrO₃ thin films.

Y-doped BaZrO₃ material suitable for sensing devices can be deposited by thin film technologies, such as sputtering and pulsed laser deposition (PLD). Thin films demonstrated the potential to fabricate mass produced devices with very small dimensions. Ba deficiency is observed in all deposited layers, however, the mechanism for this effect is still poorly understood in these thin films. Initial results appear to indicate that the Ba is more easily backspattered/etched from the surface it has been deposited on during ion bombardment, leading to the Ba deficiency. Sputtered films have a higher sensitivity towards humidity at lower temperature ($T = 400\text{ }^{\circ}\text{C}$) with fast sensor response (τ_{60}) between 6 to 27 s and an average life time of 12 weeks. PLD films yielded more stoichiometric films with sensor response (τ_{60}) between 17 to 56 s and 1 year lifetime even at higher temperature ($500\text{ }^{\circ}\text{C} \leq T \leq 650\text{ }^{\circ}\text{C}$). Thin film devices produced by both methods were highly selective to water vapor at high temperature. Therefore, yttrium-doped barium zirconate (Y-doped BaZrO₃ or YBZO) is a promising material for fast, sensitive, selective, and stable high temperature ($400\text{ }^{\circ}\text{C} \leq T \leq 650\text{ }^{\circ}\text{C}$) humidity sensors.

II.C. Microhotplate devices

Description/Rationale

A microhotplate platform that integrates a controllable heater, temperature measurement, an interdigitated electrode, and compatibility with very harsh-environments is needed for high-performance gas sensors. Many gas sensors display changes in sensitivity, selectivity, response, etc, with changes in operating temperature. Therefore, a system with rapid temperature control is needed to stabilize the operating temperature of the sensing film when used in exhaust stream applications. An efficient temperature control scheme is also desired to make the sensors compatible with power requirements of common sensor communications buses. A microhotplate platform able to control the film temperature, at high temperatures, and allow measurements of the film electrical properties is being developed.

Results and Discussion

Three separate microhotplate geometries have been developed and used across the course of this project, and included the 1st and 2nd generation structures, which was designed primarily for ease of fabrication and for use in testing the gas sensing properties of the sensing films. In addition, a 3rd generation microhotplate structure was also investigated, developed, and characterized, which was designed to be a suspended membrane high-performance microhotplate structure. This report will focus on the 3rd generation microhotplate devices, and the design and simulation processes used to optimize the design, the chosen layout, and characterization results from fabricated microhotplate structures. The primary goals for the 3rd generation microhotplates included 1) temperature uniformity, 2) ability to reach temperatures $> 600\text{ }^{\circ}\text{C}$, 3) electrodes for a variety of measurements (IDE, van der Pauw), and 4) low thermal mass (rapid heating with low power dissipation). We leveraged PI Solzbacher's experience and designs which have been reported in the literature⁶⁰⁻⁶³.

The microhotplate (MHP) design was created to be compatible with using SiC thin films as the heater layer. Use of SiC has substantial benefits for the fabrication and functionality of the MHP, which include compatibility with bulk micromachining, high strength, excellent thermal conductivity, and chemical inertness. For bulk micromachining, the SiC thin film acts as an etch stop for anisotropic KOH etch processes. This allows etching from the backside of the Si wafer

to the SiC layer, which makes very thin (typically 1 μm) microhotplates, and achieves very reliable hotplate thickness. This supports having microhotplates with very low thermal mass, but continue to be quite rugged. As we have previously reported, we were only able to obtain very limited amounts of 3C-SiC deposited on Si wafers, and the variability of physical and electrical properties of this films compromised our ability to use them for reliable microhotplate devices. Availability of high-quality SiC films is seen as a critical need for high-temperature and harsh-environment microhotplate structures and sensors going forward.

The actual sensor design has eight bridges connected to the hotplate. The suspended structure is achieved using front and back side micro-machining. Fig. 41(a) is a schematic representation of the whole device. The back side etched cavity is indicated by dashed-lines. Only six of these eight bridges are needed for the new metal oxide gas sensor generation and its functionality. The other two bridges are used for Hall measurements on the sensing film, whereby four separate point electrodes are needed. The Hall measurements serve *e.g.* for the identification of the charge carrier's mobility or density. For this Hall sensor design the two unused bridges serve for the new RTD, whereby the four bridges, used for the former RTD and the IDE structure, are needed for connecting the four point electrodes of that sensor design, as shown in Fig. 41(b).

The presented micro gas sensor detection principle is based on measuring the gas dependent change in electrical conductivity of metal oxide films. For that reason an IDE structure is sputter deposited in the center of the hotplate. Close to this interdigitated comb structure a resistive temperature device (RTD) is used for controlling the temperature of the hotplate, thus the sensing film. The gas detecting metal oxide film is sputtered above the IDE and the RTD. In the process, it has to be borne in mind, that there is no overlapping of the gas sensing film with the Pt heater contacts (hc). Otherwise there would be a short over the sensing film, and the SiC-based micro heater would not work anymore. Therefore an Si_3N_4 layer is deposited on the top as a final layer, and is only opened in that specific area. The plan-view of the microhotplate structure and the bond pad assignments used are presented in Fig. 41(b).

Fig. 41. CAD designs for the microhotplate structure that was simulated using finite element analysis methods, and includes (a) an oblique perspective showing the bulk micromachined cavity below the MHP, and (b) a plan-view identifying bond pads and the IDE structures.

The design requirements for the microhotplate structures pursued by this project are listed in Table 10. The heater efficiency as well as the power consumption play an important role, both depending on geometric size, material properties and the quantity of different power losses. The operating temperature range should be large enough for being usable in as many gas sensor applications as possible. Furthermore, the thermal time constant should be small enough to allow different modes of operation. The temperature inhomogeneity across the sensing film should not exceed a variation between 5 and 10 °C, since the metal oxide characteristics vary with temperature. This would comply with a 0.5–1% deviation by 900 °C operating temperature of the hotplate. The comparably large chip and heater size requirements provide enough space for a proper IDE structure for contacting the metal oxide. Thereby, the use of a large bandwidth of different metal oxides with different specific resistances is ensured. The operating voltage should be in the range of battery operation capabilities, *i.e.* the device is conceivable as a hand-held one. The technical requirements for the novel sensor concept of Table 10 are still on a level with state of the art.

Table 10. Specifications used for the design and simulation of the microhotplate.

Property	Quantity	Unit
Heater efficiency	> 9	°C/mW
Power consumption	< 100	mW
Operating temperature range	RT ... 900	°C
Thermal response time	< 100	ms
Temperature variance across metal oxide	±5 ... 10	°C
Size chip	< 5 × 5	mm ²
Size heater	< 500 × 500	μm ²
Operating voltage	1 – 5	V
Sensing electrode structure	flexible/IDE	

The details regarding materials choices, mesh geometries, boundary conditions, and simulation methodologies are beyond the scope of this report, but are contained in the Thesis for Karsten Kühn, which will be submitted to the DOE. The simplified geometry used for the microhotplate structure, and the chosen mesh are presented in Fig. 42 (a). A representative plot of the temperature distribution across the MHP when a 2 VDC bias is placed across the heater contacts is presented in Fig. 42(b). The octagonal microhotplate heater area is observed to be relatively uniform in temperature, and a strong temperature gradient exists along the 2 bridge elements that support the hotplate area. Even with this quite modest bias, the microhotplate was simulated to achieve a temperature > 400 °C. The design was then investigated and optimized by examining the effect of the bridge length and bridge width on the temperature uniformity and power dissipation needed to achieve temperatures in the desired range (400 °C < T < 800 °C).

(a)

(b)

Fig. 42. FEA simulations were used to investigate the properties of microhotplate, and this figure includes (a) the mesh used for the octagonal microhotplate, and (b) some representative data showing the temperature distribution of a microhotplate with a 2 VDC bias achieving a maximum temperature of $> 400\text{ }^{\circ}\text{C}$.

Bridge widths of 40, 50 and 60 μm were used for the simulations to optimize the MHP design, and bridge lengths were also varied from 0.5, 0.75, to 1 mm. In addition, biases from 2 to 6 VDC were applied to determine the effect of biases on the maximum temperature, and the temperature distribution across the device. The maximum temperature and distributions are expected to change, as the relative contributions of heat transport by conduction, convection, and radiation change with different dependencies on the MHP temperature. Overall, there was rarely more than a 100 $^{\circ}\text{C}$ difference in the maximum temperature achieved between the various geometries, and as subsequent data indicates, temperatures of $> 1000\text{ }^{\circ}\text{C}$ are predicted for biases of 6 VDC. While the bridge length and width do have strong influences on the maximum temperature achieved, most of these variations can be compensated for by changing the applied bias on the heater. These results suggest that the microhotplate design has a great deal of latitude available in the design and processing parameters, while still meeting the general power and temperature requirements.

Fig. 43. The maximum hotplate temperature is plotted as a function of bridge length for 0.5, 0.75, and 1 mm bridge lengths and for bridge widths of 40, 50, and 60 μm for applied biases of (a) 2 VDC, (b) 3 VDC, (c) 4 VDC, and (d) 5 VDC.

The temperature uniformity across the microhotplate and bridge supports is presented in Fig. 44. The linear behavior along the bridges changes into a parabolic one across the MHP, and have been observed in prior publications^{60,64}. The maximum temperature, temperature profile, and gradient are affected by the bridge width. The simulated temperature distributions across the MHP with an area of 0.17 mm^2 varies around 10 to 25 °C straight between the heater contacts and approximately 2 to 5 °C in transverse direction (across the hotplate, but in a direction orthogonal to the bridge elements). The larger 10 to 25 °C variation across the hotplate in the direction of the support bridges is larger enough that it could result in non-uniformity in the response for the gas sensing film. For the final design with 8 bridges, the temperature variation will be more consistent, due to heat transport down the additional bridges. This suggests that the sensing layer should be maintained closer to the central region of the hotplate to achieve the desired temperature uniformity.

Fig. 44. Plot of the temperature as a function of position between the 2 bond pads as presented in Fig. 42(b), where the center of the microhotplate is at 1 mm, and has a relatively constant temperature before transitioning into the bridge regions on each side, which show a strong temperature gradient.

An overall simulation of the temperature of the microhotplate with an applied bias of 5 VDC is presented in Fig. 45. The simulations suggest this device is able to exceed temperatures of 800 °C with very modest applied powers (5 VDC and 85 mW of power). These characteristics exceed the specified design criteria, and should enable this design to be compatible with portable sensor applications, sensors for transportation (cars), and for stationary power plants. In addition, the time constants for temperature changes were also simulated, and found to be in the 35 to 70 ms range for temperature changes of $\gg 100$ °C, which suggests the hotplates could be used for temperature programmed measurements which have shown a great deal of promise for improving the selectivity of metal oxide sensors. The stress resulting from thermal expansion of different materials and from temperature gradients were also investigated. While the developed stresses were found to be significant, the compliant nature of the suspended microhotplate did not achieve stresses greater than what would likely rupture the device. These results suggest that thermal degradation mechanisms will more likely compromise the high-temperature stability and lifespan of the device, than problems arising from mechanical stresses.

Fig. 45. FEA simulation of the temperature distribution of the full microhotplate design that includes the 8 support bridges used to apply power to the heater, measure the gas sensing film, measure the temperature, and enable Hall measurements in the van der Pauw geometry.

Final CAD designs for the final 3rd generation microhotplate as fabricated by MSF are presented in Fig. 46. The microhotplate die is $5 \times 5 \text{ mm}^2$ in size. We have implemented a buried poly-Si heater to reach temperatures of up to $900 \text{ }^\circ\text{C}$ in air based on thermo-electro-mechanical simulations presented previously. The hotplate is expected to consume $< 100 \text{ mW}$ with a thermal response time of $< 100 \text{ ms}$. The heated membrane area is 1.75 mm^2 . The gas sensitive layers will be deposited on top of the IDE structures using a shadow mask.

The microhotplates also have three different IDE geometries, including a single electrode pair with $1000 \text{ }\mu\text{m}$ spacing, 3 electrode pairs with $300 \text{ }\mu\text{m}$ spacing, and 7 electrode pairs with $100 \text{ }\mu\text{m}$ spacing. The number of electrode pairs and spacing mimic our first generation hotplate structures, which are used for current tests. The devices also include Hall measurement and spiral IDE structures besides the typical IDE structures as depicted in Fig. 47 (a-b). The masks and designs were submitted to the Microtechnology Services Frankfurt (MSF), a commercial MEMs foundry in Germany for fabrication. The MHP structures were implemented with buried polysilicon heaters due to the unavailability of SiC.

Fig. 46. Microhotplate design with single electrode pair Pt IDE. A buried poly-Si layer acts as the heater layers with a poly-Si RTD measuring the temperature of the microhotplate. The die is $5 \times 5 \text{ mm}^2$ with the heated membrane area being 1.75 mm^2 .

Fig. 47. (a) Spiral IDE structure and (b) Hall structures on the microhotplate die. The hall structures will help enable us gain better understanding of sensing mechanisms with *in situ* measurements.

Having finalized the design, we expect to finish fabrication of these hotplates during the next quarter and to commence testing our gas sensitive layers soon thereafter. In addition, we are nearing completion of our Hall measurement system, that will enable these measurements for samples at high temperatures and with the same range of test gases as available on our current gas sensor test station. With the ability to operate gas sensitive layers at elevated temperatures ($> 500\text{ }^{\circ}\text{C}$) with a buried heater layer, we should be able to gain a better understanding of how these thin film materials behave in these harsh environments by studying their carrier concentration, mobility, and electrical characteristics.

The overall concept for the architecture changes are to simplify the set of materials that are exposed to the high temperatures present on the hotplate region, and to achieve better electrical isolation for the heater. This design uses highly-doped poly-silicon as conducting lines and for the heater, and limits metal layers on the microhotplate to those used for the interdigitated electrodes, which are deposited on top of a Si_3N_4 layer to avoid metallurgical reactions. Also, because this design is likely to be compatible with processes available in many foundries, multiple sources are available to fabricate parts, which alleviates risk in getting devices produced. This design also uses a combined SiO_2 and Si_3N_4 suspended membrane structure to support the heater and electrodes for the gas sensor. These films will be relatively thin ($\sim 1\text{ }\mu\text{m}$) so will keep the thermal mass of the microhotplate very small, which enables it to change temperatures very quickly. In addition, these materials can be used as etch stop layers for bulk micromaching process based on KOH etching. These allow for much simpler and more precise control of the microhotplate thickness and thermal characteristics. A cross-sectional diagram of the layer structure is presented in Fig. 48.

Fig. 48. A cross-sectional diagram of the layers used to create the 3rd generation microhotplate device. The layers include (red) silicon substrate, (light blue) SiO_2 , (green) Si_3N_4 , (orange) poly-silicon, (purple) Si_3N_4 , (grey) Pt, and (blue) the gas sensing layer.

The devices received from MSF did not have the top-side isolation etch process performed, so the hotplate remained on a continuous membrane of Si_3N_4 . An optical micrograph of the microhotplates is presented in Fig. 49, where the transparent areas surrounding the die is the Si_3N_4 and SiO_2 films. Quick tests to determine the power needed to heat the device have shown that even with the full membrane in place, the device can be heated to glowing faintly red with 0.25 W. We also anticipate that the devices will be able to achieve rapid temperature changes, which will allow temperature cycling, a technique that has proven very useful in improving the overall sensor selectivity. In addition, there are contacts for Hall measurements from sensing films at high temperatures, and a variety of IDE contacts that will allow measuring films with a large range of resistivities, and to investigate the effects of IDE geometries on the sensor response.

Fig. 49. Plan-view micrograph of a 3rd generation microhotplate using a polysilicon heater and RTD. The IDE is Pt with a spacing of 1 mm (0.3 and 0.1 mm where also fabricated). The microhotplates glowed faintly red when 0.25 W is applied from a DC power supply.

The characterizations of the hotplates are being carried out jointly by the University of Utah and Saarland University, Germany. Detailed results on the above mentioned characteristics are awaited from the collaborating lab. Preliminary results characterizing the temperature coefficient of resistance (TCR) for the polysilicon RTD and polysilicon heater are presented below in Fig. 50 (a-b), respectively. Measuring the RTD resistance as a function of chamber temperature, we see a non-linear response across the temperature range (50 to 500 °C). Measurements did not exceed 500 °C as the nitride membrane delaminated. We are hopeful the delamination will not occur for the devices where the holes are etched in the Si₃N₄ membrane, that allow deformation to relieve stress in the devices. Fig. 50(a) shows two set of measurements (Pass 1-3 and Pass 4-6). The arrows point whether the temperature was ramped up/cooled down. The time difference between Pass 1-3 and Pass 4-6 was two days. For the first set of measurements (Pass 1 or Pass 4), the RTD resistance is lower than for future cycles (Pass 2-3 or Pass 4-5). Also the overall TCR of the RTD is lower and more varying compared to the heater TCR shown later in Fig. 50(b). The use of RTD as a heater control is not recommended due to the non-linear response as well as low TCR compared to the heater.

Fig. 50. The resistance of the (a) polysilicon RTD and (b) heater structures were characterized as a function of temperature for the microhotplate devices.

The heater resistance was measured after the RTD resistance and shows a similar resistance-temperature cycling profile. The heater resistance (720 Ω) is much lower than the RTD resistance (44.2 k Ω). Also, the heater resistance has a linear profile in the measurement range (200 to 500 °C) when compared to the RTD resistance. The TCR for RTD was measured in the range 300 to 500 °C due to the non-linear response at lower temperatures. It was observed that the TCR for heater ($\sim 0.04\% / ^\circ\text{C}$) is larger compared to the RTD resistance ($0.027\% / ^\circ\text{C}$). Also the variation in average TCR from sensor to sensor is lower for the heater (0.038 ± 0.002) compared to the RTD resistance (0.027 ± 0.012). Hence we recommend using the heater resistance for temperature control.

The MHPs were also used in conjunction with an sputter deposited In_2O_3 film to characterize the ability to measure gas sensor responses with these devices while using the hotplate to heat the sensing film. 150 nm thick In_2O_3 layers and Au promoter layers were deposited on the 3rd generation microhotplate die and were exposed to 25 ppm NO_x as a function of operating voltages. The sensor was tested using 10, 12, 14, and 16 VDC, as for each of these applied biases, the microhotplate glowed faintly. The faint red glow was perceived at an operating voltage of 10 VDC suggesting the operating temperature was approximately ~ 600 °C and at 16 VDC, the die was clearly glowing red suggesting a temperature > 700 °C. Fig. 51 presents the measured time constants and gas sensor responses for each of the operating voltages tested. The microhotplate consumed 120, 170, 210, and 250 mW of power, respectively, at the operating biases of 10, 12, 14, and 16 VDC. These very lower power consumptions despite the lack of the MHP isolation etch through the nitride strongly suggest that the device has very good power efficiency for achieving high temperatures, which is very important for mobile, transportation, and potentially wireless versions of the sensor architecture.

Fig. 51. The time constants and gas sensor response are presented for a 150 nm In_2O_3 film with Au promoter layer deposited on a 3rd generation microhotplate structure. The gas sensing characteristics were measured using the microhotplate to heat the sensing film, and used supply voltages of 10, 12, 14, and 17 VDC.

The In_2O_3 sensors show high sensitivity (> 50) to 25 ppm NO_x with quick response (< 11 s). The time constants modeled using two time constants (τ_{initial} and τ_{final}) suggested two potentially overlapping NO_x sensing mechanisms occurring on the In_2O_3 thin film. We have presented τ_{initial} data which accurately represents the initial rate of adsorption/desorption of NO_x species on the In_2O_3 surface. Since the correlation between operating voltages and temperature is unknown, we cannot accurately compare the performance of films deposited on microhotplates to thin films tested by passive heating. But the results suggest, the sensor response to NO_x for microhotplates dies is quicker (~ 5 s) compared to passively heated films (~ 10 s). Also the NO_x response attains saturation across the operating voltage, not seen in In_2O_3 thin films with passive heating. This suggests the NO_x adsorption/desorption equilibrium is attained quickly in microhotplate sensors compared to passively heated sensors. Further tests are ongoing to characterize the performance of In_2O_3 layers deposited on microhotplate dies, but these results clearly suggest working devices with good power consumption and sensing characteristics despite the continuous Si_3N_4 membrane. Therefore, these devices are very promising, and warrant significantly more attention to characterize their performance, and further optimize their properties.

Conclusions

Three generations of microhotplates were developed, fabricated, and characterized for this project. The 1st and 2nd generations devices were test structures focused on ease of fabrication, and accurate measurements of the gas sensor response for sensing films. The 3rd generation microhotplate design is a high-performance MHP based on using suspended membranes to achieve high temperatures, low thermal time constants, and low power consumption. The 3rd generation designs were extensively simulated using finite element analysis tools, based on a SiC heater layer. The simulations indicated that the MHP could reach temperatures > 1000 °C with 5 or 6 VDC, and had lower thermal time constants, and therefore met the design criteria. Unfortunately, we were never able to acquire reliable 3C-SiC material, so could not implement

the design using this material. Our design was also created such that it could be implemented using a membrane made using layers of SiO_2 and Si_3N_4 . This design was successfully implemented, and preliminary tests indicate it can achieve temperatures $> 600^\circ\text{C}$ with an applied bias of less than 20 VDC. This device has not had the membrane isolation etch performed, and therefore these results should be significantly lower than what the completed device will achieve.

In addition, the 3rd generation microhotplates were used for gas sensor tests with In_2O_3 films, using the built-in heater to control the sensor temperature. These sensors were found to have sensitivities similar to those that were reported when using the external heater on the gas sensor test station. This suggests that the sensing films were at temperature in the 400 to 700 $^\circ\text{C}$ range, which is very consistent with our project goals. The good sensitivities of these sensors, and the very fast time constants suggest that these sensor *systems* have a lot of potential for development into commercial products.

II.D. Gas Sensor Test Station

All of the gas sensor measurements collected during this project utilized a custom-built gas sensor test station that was designed and implemented by Clayton Butler as a Masters of Science project. Details regarding this system are beyond the scope of this report, but we do want to acknowledge the importance of this system for our research. An electronic version of Mr. Butler's thesis will be provided to the DOE, such that the details, operating ranges, and pertinent characteristics of this system are available.

III. Proposal Milestones:

Proposal Milestones: Phase I	Anticipated completion date	Actual completion date
<u>Thrust I - Semiconducting metal oxides</u> <ul style="list-style-type: none"> Initial thin films of In_2O_3, Ga_2O_3, and NiO deposited by RF sputter deposition from ceramic targets (Oxidized Si, or quartz substrates) Characterization of initial films by EDX (composition), AFM (surface morphology), XRD (crystallography and structure), four-point probe, and Hall measurements (electrical properties) Measure gas sensing characteristics (sensitivity, selectivity, response time, recovery time, stability) as functions of temperature, pressure, and gas concentration in a controlled ambient furnace High temperature anneal ($T > 800^\circ\text{C}$) in oxidizing and reducing ambients Characterize and measure gas sensitivity properties again Improve films (based on gas sensitivity) by variation of sputter deposition parameters (i.e. process pressure, oxygen partial pressure, power, substrate temperature, etc), using the described development loop Investigate gas sensing improvement through controlled additions of promoter materials (e.g. Ti and/or TiO_2) incorporated via cosputtering 	09/30/05 12/31/05 03/31/06 04/28/06 06/09/06 07/03/07 07/03/07	09/30/05 12/31/05 03/31/06 06/23/06 10/18/06 12/31/07: Continuous during project 12/31/07: Continuous during project 10/31/05
<u>Thrust II - Electrochemical oxides and sulphides</u> <ul style="list-style-type: none"> Procurement of dedicated sputter deposition system for use with sulphide and Ba materials (~ 6 months) Initial deposition of $\text{BaZr}_{(1-x)}\text{Y}_x\text{O}_{(3-x/2)}$ (and $\text{BaCe}_{(2-x)}\text{Ca}_x\text{S}_{(4-x/2)}$) thin films (note that oxides materials will be investigated first due to sulfur volatilization from the vacuum chamber walls) Characterization of films by EDX (composition), AFM (surface morphology), XRD (crystallography and structure), and variable temperature impedance spectroscopy (electrical properties) Measure gas sensing characteristics (same as listed above). High temperature anneal ($T > 800^\circ\text{C}$) in H_2S and Ar ambients Characterize and measure gas sensitive properties again Layer refinement by controlling dopant concentration (Y and Ca, respectively), and controlling deposition parameters (same as listed for semiconductive layers above except O_2 used during deposition). 	10/31/05 01/09/06 03/20/06 05/29/06 06/26/06 08/07/06 07/09/07	12/31/05 03/31/06 06/19/06 09/24/06 10/15/06 12/31/07: Continuous during project
<u>Thrust III - Micro hotplate development</u> <ul style="list-style-type: none"> Deposition and characterization of micro hotplate layers including high temperature conductors (e.g. TiWN), insulators (e.g. Si_3N_4) Measure residual stress in micro hotplate layers, and refine deposition process to achieve balanced stresses at operating temperatures Develop photomasks and lithography process for microfabrication of hotplate structures Use 3C-SiC coated Si substrates, conductive and insulating layers, and bulk and surface micromachining processes to fabricate microhotplates. Characterize hotplate performance (high temperature lifetime and stability, heater resistance and temperature coefficient of resistivity (TCR), heater power requirements, and failure analysis) Design and fabrication process improvements to improve micro hotplate characteristics, lifetime, and stability 	09/30/05 03/20/06 04/17/06 10/02/06 01/02/07 07/09/07	09/30/05 03/31/06 06/30/06 09/12/07: 2 nd Gen 08/27/09: Si_3N_4 11/15/07: 2 nd Gen 10/25/09: Si_3N_4 07/09/08: began Si_3N_4 design

Proposal Milestones: Phase II	Anticipated completion date	Actual completion date
<u>Carried Over Phase I Milestones:</u>		
<u>Thrust I - Semiconducting metal oxides</u>		
• Improve films (based on gas sensitivity) by variation of sputter deposition parameters (i.e. process pressure, oxygen partial pressure, power, substrate temperature, etc), using the described development loop	07/03/07	12/15/07
• Investigate gas sensing improvement through controlled additions of promoter materials (e.g. Ti and/or TiO ₂) incorporated via cosputtering	07/03/07	12/01/07
<u>Thrust II - Electrochemical oxides and sulphides</u>		
• Layer refinement by controlling dopant concentration (Y and Ca, respectively), and controlling deposition parameters (same as listed for semiconductive layers above except O ₂ used during deposition).	07/09/07	03/10/08
<u>Thrust III - Micro hotplate development</u>		
• Use 3C-SiC coated Si substrates, conductive and insulating layers, and bulk and surface micromachining processes to fabricate microhotplates.	10/02/06	09/12/07: 2 nd Gen 08/27/09: Si ₃ N ₄
• Characterize hotplate performance (high temperature lifetime and stability, heater resistance and temperature coefficient of resistivity (TCR), heater power requirements, and failure analysis	01/02/07	11/15/07: 2 nd Gen 10/25/09: Si ₃ N ₄
• Design and fabrication process improvements to improve micro hotplate characteristics, lifetime, and stability	07/09/07	07/09/08: began Si ₃ N ₄ design
<u>Phase II Milestones:</u>		
<u>Thrust III - Integration of sensing layers with micro hotplates - All investigators:</u>		
• Deposition, patterning, and contacts for optimized sensing layers on micro hotplates	02/04/08	10/28/09: for In ₂ O ₃ on Si ₃ N ₄
• Lifetime and stability testing of integrated sensor die in inert and reactive gas ambients with subsequent failure analysis	04/07/08	11/09/09: for In ₂ O ₃ on Si ₃ N ₄
• Characterization of gas sensing properties (as listed previously) utilizing sensor heating element for temperature control in synthetic gas ambients	05/05/08	11/21/09: for In ₂ O ₃ on Si ₃ N ₄
• Refinement of gas sensing properties (layer optimization), and device lifetime (failure analysis)	06/15/08	12/31/09: for In ₂ O ₃ on Si ₃ N ₄

Proposal Milestones: Project Extension	Anticipated completion date	Actual completion date
<p><u>4th Year Phase I Milestones:</u></p> <p><u>Thrust I - Semiconducting metal oxides</u></p> <ul style="list-style-type: none"> Preliminary investigation of TiWO_x and WO_x Extrinsic doping of metal-oxides to improve gas sensing and stability at high temperatures <p><u>Thrust II - Electrochemical oxides and sulphides</u></p> <ul style="list-style-type: none"> Fabricate rare earth oxide or alkaline earth oxide (inert) and transition metal (active) multi-cation complex oxides. Anticipated structures include perovskites Measure conductivity of multi-cation materials as a function of temperature and atmosphere Explore gas sensing properties of dense and porous samples multi-cation materials <p><u>Thrust III - Micro hotplate development</u></p> <ul style="list-style-type: none"> Characterize hotplate performance (high temperature lifetime and stability, heater resistance and temperature coefficient of resistivity (TCR), heater power requirements, and failure analysis) Design and fabrication process improvements to improve micro hotplate characteristics, lifetime, and stability <p><u>4th Year Phase II Milestones:</u></p> <p><u>Thrust III - Integration of sensing layers with micro hotplates - All investigators:</u></p> <ul style="list-style-type: none"> Deposition, patterning, and contacts for optimized sensing layers on micro hotplates Lifetime and stability testing of integrated sensor die in inert and reactive gas ambients with subsequent failure analysis Characterization of gas sensing properties (as listed previously) utilizing sensor heating element for temperature control in synthetic gas ambients Refinement of gas sensing properties (layer optimization), and device lifetime (failure analysis) Characterization of the gas sensitive properties for metal oxides and electro-ceramics in complex gas mixtures Characterization of layer long-term stability and drift, identification of failure modes and subsequent improvement of sensing materials in gas mixtures Improve stability (reduce etching) of In_2O_3 in reducing gas mixtures 	<p>12/19/08</p> <p>03/20/09</p> <p>05/15/09</p> <p>03/27/09</p> <p>04/17/09</p> <p>01/02/07</p> <p>07/09/07</p> <p>02/04/08</p> <p>04/07/08</p> <p>05/05/08</p> <p>06/15/08</p> <p>02/27/09</p> <p>04/17/09</p> <p>05/15/09</p>	<p>12/10/08</p> <p>03/24/09</p> <p>05/15/09 for BaZrO_3</p> <p>08/19/09 for BaZrO_3</p> <p>11/09/09 for BaZrO_3</p> <p>11/15/07: 2nd Gen 10/25/09: Si_3N_4</p> <p>07/09/08: began Si_3N_4 design</p> <p>10/28/09: for In_2O_3 on Si_3N_4</p> <p>11/09/09: for In_2O_3 on Si_3N_4</p> <p>11/21/09: for In_2O_3 on Si_3N_4</p> <p>12/31/09: for In_2O_3 on Si_3N_4</p> <p>12/03/09: for In_2O_3 on Si_3N_4</p> <p>Delayed due to acquiring 3C-SiC</p> <p>Incomplete: could not decrease etching despite many experiments</p>

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VI. References/Bibliography

References

- 1 N. Barsan and U. Weimar, Journal of Physics: Condensed Matter **15**, 813-39 (2003).
- 2 M. Fleischer and H. Meixner, Sensors and Actuators B (Chemical) **B52**, 179-87 (1998).
- 3 N. Yamazoe and K. Shimano, Sensors and Actuators: B. Chemical **128**, 566-73 (2008).
- 4 F. Linder, "Diesel Exhaust Emissions," (2007).
- 5 X. Chen, L. Rieth, M. S. Miller, and F. Solzbacher, Sensors and Actuators, B: Chemical **137**, 578-585 (2009).
- 6 C. Butler, Thesis, University of Utah, 2008.
- 7 G. J. Li and S. Kawi, Materials Letters **34**, 99-102 (1998).
- 8 N. Barsan and U. Weimar, Journal of Electroceramics **7**, 143-67 (2001).
- 9 B. Sasi, K. G. Gopchandran, P. K. Manoj, P. Koshy, P. P. Rao, and V. K. Vaidyan, Vacuum **68**, 149-54 (2003).
- 10 I. Hotovy, J. Huran, P. Siciliano, S. Capone, L. Spiess, and V. Rehacek, Sensors and Actuators B: Chemical **103**, 300-311 (2004).
- 11 M. Madou, *Chemical sensing with solid state devices* (Academic Press, Boston, 1989).
- 12 *Solid State Gas Sensing; Vol.*, edited by E. Comini, G. Faglia, and G. Sberveglieri (Springer, New York, 2009).
- 13 I. Simon, N. Barsan, M. Bauer, and U. Weimar, Sensors and Actuators B (Chemical) **B73**, 1-26 (2001).
- 14 M. Frietsch, F. Zudock, J. Goschnick, and M. Bruns, Sensors and Actuators B (Chemical) **B65**, 379-81 (2000).
- 15 H. Steffes, C. Imawan, F. Solzbacher, and E. Obermeier, in *Fabrication parameters and NO₂ sensitivity of reactively RF-sputtered In₂O₃ thin films*, The Hague, Netherlands, 2000 (Elsevier), p. 249-53.
- 16 Jeong, J. Vac. Sci. Technol. A **14** (1996).
- 17 G. Korotcenkov, V. Brinzari, A. Cerneavski, M. Ivanov, V. Golovanov, A. Cornet, J. Morante, A. Cabot, and J. Arbiol, Thin Solid Films **460**, 315-323 (2004).
- 18 A. Gurlo, M. Ivanovskaya, N. Barsan, M. Schweizer-Berberich, U. Weimar, W. Gopel, and A. Dieguez, Sensors and Actuators B-Chemical **44**, 327-333 (1997).
- 19 N. Yamazoe, Sensors and Actuators B: Chemical **5**, 7-19 (1991).
- 20 M. Haruta, Catalysis Today **36**, 153-166 (1997).
- 21 H. Steffes, C. Imawan, F. Solzbacher, and E. Obermeier, in *Enhancement of NO₂ sensing properties of In₂O₃-based thin films using an Au or Ti surface modification*, Copenhagen, Denmark, 2001 (Elsevier), p. 106-12.
- 22 K. H. Choi, B. Y. Coh, and H. I. Lee, Catal. Today **44**, 205-213 (1998).
- 23 M. A. Chesters and G. A. Somorjai, Surface Science **52**, 21-28 (1975).
- 24 G. C. Bond and D. T. Thompson, Catalysis Reviews-Science and Engineering **41**, 319-388 (1999).
- 25 W.-H. Tao and C.-H. Tsai, Sensors and Actuators B: Chemical **81**, 237-247 (2002).
- 26 M. Penza, G. Cassano, R. Rossi, A. Rizzo, M. A. Signore, M. Alvisi, N. Lisi, E. Serra, and R. Giorgi, Applied Physics Letters **90**, 103101-3 (2007).
- 27 M. Penza, C. Martucci, and G. Cassano, Sensors and Actuators B: Chemical **50**, 52-59 (1998).

28 *Catalysis by Gold (Catalytic Science)*; Vol. 6, edited by G. C. Bond (Imperial College
Press, 2006).

29 D. Haridas, K. Sreenivas, and V. Gupta, *Sensors and Actuators B: Chemical* **133**, 270-
275 (2008).

30 G. Korotcenkov, V. Brinzari, Y. Boris, M. Ivanova, J. Schwank, and J. Morante, *Thin
Solid Films* **436**, 119-126 (2003).

31 L. Lietti, I. Nova, E. Tronconi, and P. Forzatti, *Catalysis Today* **45**, 85-92 (1998).

32 M. Devadas, O. Krocher, M. Elsener, A. Wokaun, N. Soger, M. Pfeifer, Y. Demel, and L.
Mussmann, *Applied Catalysis B: Environmental* **67**, 187-196 (2006).

33 P. G. Ashmore and B. P. Levitt, *Nature* **176**, 1013-1015 (1955).

34 T. Automotive, (2009).

35 T. Hryniewicz, R. Rokicki, and K. Rokosz, *Corrosion* **64**, 660-5 (2008).

36 P. Lowery, "Comparing the characteristics of surface passivated and electropolished
316L stainless steel," (2009).

37 G. Marbán, R. Antuña, and A. B. Fuertes, *Applied Catalysis B: Environmental* **41**, 323-
338 (2003).

38 S. Kannan, L. Rieth, and F. Solzbacher, *Sensors and Actuators B (Chemical)* (submitted).

39 M. J. Toohey, *Sensors and Actuators B: Chemical* **105**, 232-250 (2005).

40 X. Vilanova, E. Llobet, J. Brezmes, J. Calderer, and X. Correig, *Sensors and Actuators B:
Chemical* **48**, 425-431 (1998).

41 H. Gourari, M. Lumbreras, R. Van Landschoot, and J. Schoonman, *Sensors and
Actuators B: Chemical* **58**, 365-369 (1999).

42 S. Pitcher, J. A. Thiele, H. Ren, and J. F. Vetelino, *Sensors and Actuators B: Chemical*
93, 454-462 (2003).

43 M. Liess, *Thin Solid Films* **410**, 183-187 (2002).

44 B. M. Kulwicki, *Journal of the American Ceramic Society* **74**, 697-708 (1991).

45 E. Traversa, in *Ceramic sensors for humidity detection: the state-of-the-art and future
developments*, Switzerland, 1995, p. 135-56.

46 P. Shuk and M. Greenblatt, in *Solid electrolyte film humidity sensor*, Netherlands, 1998
(Elsevier), p. 229-33.

47 S. Xiaolei, C. Qi, F. Ji, K. Varahramyan, and J. Hai-Feng, *Sensors and Actuators B
(Chemical)* **129**, 241-5 (2008).

48 E. Massera, G. Di Francia, A. Castaldo, I. Nasti, L. Quercia, and I. Rea, *Sensors and
Actuators B (Chemical)* **111-112**, 135-9 (2005).

49 K. Arshak, K. Twomey, and D. Egan, *Sensors* **2**, 50-61 (2002).

50 W. Wang and A. V. Virkar, *Journal of Power Sources* **142**, 1-9 (2005).

51 W. Wang and A. V. Virkar, *Sensors and Actuators B (Chemical)* **B98**, 282-90 (2004).

52 C. D. Savaniu, J. Canales-Vasquez, and J. T. S. Irvine, *Journal of Materials Chemistry*
15, 598-604 (2005).

53 K. Katahira, Y. Kohcki, T. Shimura, and H. Iwahara, *Solid State Ionics, Diffusion &
Reactions* **138**, 91-8 (2000).

54 V. P. Gorelov, V. B. Balakireva, Y. N. Kleshchev, and V. P. Brusentsov, *Inorganic
Materials* **37**, 535-8 (2001).

55 M. Laidoudi, I. A. Talib, and R. Omar, *Journal of Physics D (Applied Physics)* **35**, 397-
401 (2002).

56 F. M. M. Snijkers, A. Buekenhoudt, J. Coymans, and J. J. Luyten, *Scripta Materialia* **50**,

655-9 (2004).

57 D. C. Li, W. Liu, Y. Zhang, P. Yang, and C. Chen, *Solid State Communications* **131**, 235-9 (2004).

58 F. Iguchi, T. Yamada, N. Sata, T. Tsurui, and H. Yugami, *Solid State Ionics, Diffusion & Reactions* **177**, 2381-4 (2006).

59 H. Norton, *Handbook of Transducers* (Prentice-Hall, Upper Saddle River, NJ, 1989).

60 F. Solzbacher, T. Doll, and E. Obermeier, in *A comprehensive analytical and numerical analysis of transient and static micro hotplate characteristics*, Boston, MA, USA, 2003 (IEEE), p. 1856-9.

61 F. Solzbacher, C. Imawan, H. Steffes, E. Obermeier, and M. Eickhoff, in *A highly stable SiC based microhotplate NO₂ gas-sensor*, Copenhagen, Denmark, 2001 (Elsevier), p. 216-20.

62 F. Solzbacher, C. Imawan, H. Steffes, E. Obermeier, and M. Eickhoff, in *A new SiC/HfB₂ based low power gas sensor*, Basel, Switzerland, 2001 (Elsevier), p. 111-15.

63 F. Solzbacher, C. Imawan, H. Steffes, E. Obermeier, and H. Moller, in *A modular system of SiC-based microhotplates for the application in metal oxide gas sensors*, Sendai, Japan, 2000 (Elsevier), p. 95-101.

64 J. Puigcorbe, D. Vogel, B. Michel, A. Vila, I. Gracia, C. Cane, and J. R. Morante, *Journal of Micromechanics and Microengineering* **13**, 548-56 (2003).

Appendix 1: Clayton Butler's Masters Thesis

Clayton Butler's Masters thesis is included as part of this report because his thesis focused on the design, construction, and testing/validation of the gas sensor test station that was an integral part of our research effort.

CHAPTER 1

INTRODUCTION

Air pollution from fossil-fuel consuming internal combustion engines is detrimental to public health and the viability of the global environment. The Environmental Protection Agency (EPA) has identified exhaust emissions from diesel trucks, buses, and construction equipment as substantial contributors to urban air pollution. As a result, heightened attention has been focused on the need for control systems that monitor exhaust gasses and provide feedback to diesel engine management and pollution control systems. Through the use of advanced control systems and improved exhaust treatment, the amount of exhaust emissions can be reduced while improving efficiency [1], [2].

To reduce harmful exhaust emissions requires sensor feedback system to enable technologies such as selective catalytic reduction systems for NO_x reduction and exhaust particulate filtration systems. Implementing feedback control will require measuring the concentration of combustion by-products in the exhaust stream. High temperatures and aggressive gasses in the exhaust stream create a harsh environment that requires sensor devices capable of tolerating these conditions while still accurately sensing concentrations of target gasses (*e.g.*, CO, CO₂, NH₃, NO_x, hydrocarbons, H₂, H₂S, and H₂O). Measuring the exhaust gas composition downstream of catalytic converters and particle traps is needed for timely purging, maintenance or replacement, and closed loop feedback for some emission control systems.

Scientists are investigating sensor devices that meet both of these requirements by using gas

sensitive thin film in conjunction with micro-hotplate systems. To test new sensor designs and materials, a custom-made computer controlled Test Station was built to measure the gas sensing characteristics of new sensor materials and devices.

Sensing materials being investigated include oxide thin films of indium oxide (In_2O_3), gallium oxide (Ga_2O_3), nickel oxide (NiO), and electroceramic thin films such as BaZrO_3 . The variables that describe the gas sensing characteristics for these devices include: response, sensitivity, selectivity, response time, concentration range, precision, accuracy, resolution, stability, temperature dependence, and temperature range. Testing gas sensors is a critical task to determine the gas sensor response at a variety of conditions. The Test Station developed during the course of this project can control varying concentrations, flow velocities, and gas residence times of the target gasses: CO , CO_2 , NH_3 , NO_x , hydrocarbons, H_2 , H_2S and H_2O .

The design process commenced with a review of comparable testing system designs. Once a cross section of basic designs were identified, simulations were carried out for the flow of gasses, mechanical systems, and temperature controls for each design. The final design was built as a test platform for newly developed sensor designs. The completed Test Station allows for sample sensors to be exposed to individual or multiple test gasses in concentrations of less than one part per million (ppm) up to 100% concentration. The Test Station can vary the gas volumetric flow rate from 0 to 6750 standard cubic centimeters per minute (SCCM) while maintaining constant gas composition. The sensor temperature may be controlled from room temperature to a maximum of 700°C . The Test Station uses electrical probe needles, adjustable by micromanipulators to connect the sensors to external electrical measurement equipment. Functionality of gas concentration, gas flow rates, and temperature of sensor under test was confirmed separately by the use of commercial sensors.

The Test Station has proven effective for measuring the gas sensing characteristics for test devices, and has met the design criteria.

CHAPTER 2

BACKGROUND

2.1 Reducing Pollution

The desire to reduce air pollution from an ever growing number of diesel fuel internal combustion engines creates a need to reduce emissions. To accomplish this, a control network that monitors exhaust gas and provides gas concentration feedback for engine management and pollution control systems is required. As a result, industrial and academic researchers are motivated to significantly reduce harmful exhaust gas emissions from diesel engines through the development of exhaust gas sensing devices.

Sensors have a good history for decreasing internal combustion engine emissions and improving efficiency. As an example, air pollution from internal combustion engines has been reduced through the use of feedback control systems incorporating a single exhaust gas sensor. This exhaust sensor is made from a zirconium oxide and is able to detect changes in oxygen (O_2) concentration in the exhaust stream. This sensor reached widespread implementation by US automobile manufactures in response to the EPA's passage of stricter automobile emission standards in 1985 [3].

Measuring the composition of exhaust gasses requires sensor devices which can tolerate the harsh environments found in the exhaust stream while accurately sensing the concentration of target gasses. Current sensor materials are able to detect the relevant gasses of CO , CO_2 , NH_3 , NO_x ,

hydrocarbons, H_2 , H_2S , and H_2O , but have rarely been operated at temperatures greater than $500\text{ }^{\circ}\text{C}$; because current sensors are not designed for temperatures above $500\text{ }^{\circ}\text{C}$, they must be placed further down the exhaust stream where the temperatures are lower. More effective monitoring could be achieved if the sensors were placed near the combustion chamber where temperatures reach as high as $650\text{ }^{\circ}\text{C}$ [4].

2.2 Sensors

Sensors are transducers that respond to physical, chemical or biological stimuli with a measurable change in characteristic impulse response with the impulse response of a system defined as the output when presented with a very brief signal, an impulse. The response of most sensors is in the form of an electrical output, as sensors that transduce into electrical output are the easiest integration with electronics. Sensors can be classified according to the property they detect, by the measured quantity, by the type of material or technology used, and by the output signal type. This thesis concentrates on micro gas sensors, especially conductometric gas sensors made from thin film metal oxides and their application to sensing internal combustion engine exhaust gasses. The focus of this paper is conductivity sensors of metal oxides, and the development of a sensor Test Station to accurately measure their properties.

The sensor device consists of micro scale anode and cathode pads, from which emerge a pair of array electrode “fingers”. The fingers emerging from one pad overlap or “interdigitate” with the fingers emerging from the opposing pad. A pair of electrode fingers constitutes a single channel and is commonly called an interdigitated electrode (IDE). A sensor schematic showing an IDE is shown in Figure 1. A thin film of gas sensitive material is then deposited upon the electrode fingers. By

placing a voltage across the anode and cathode, current will flow through the gas sensitive material proportional to the resistance of the material. Figure 2 shows a schematic for an IDE device with a thin film gas sensitive layer.

Figure 1. Schematic of sensor interdigitated electrodes structure (IDE).
The black lines represent metal traces on a substrate. The large squares at bottom of picture are the anode and cathode pads serving as external connection points.

Figure 2. Schematic of sensor IDE with thin film gas sensitive layer (green area).

2.2.1 Microgas Sensors

Microscale gas sensors are used for detection, measurement, or analysis of gasses. These sensors use operating principles that include: mass sensitive sensors, optical sensors, thermal sensors, amperometric sensors, potentiometric sensors, and conductometric sensors. Microscale sensors have many advantages including:

- Small size compatible with compact systems.
- Low power consumption.

- Low manufacturing costs.
- Ability to incorporate micro hotplates.
- High integration/intelligence (smart sensors, self test, etc.)

2.2.2 Metal Oxide Gas Sensors

Metal oxide gas sensors are typically conductometric sensors which means they change conductivity when exposed to different concentrations of target gasses. Metal oxides are semiconductors and their change in conductivity is based on changes in the carrier concentration and/or carrier mobility of the film upon adsorption of certain gas molecules. Metal oxide gas sensors respond to oxidizing or reducing gasses via changes in conductivity due to: diffusion of reactants to the active region, adsorption of reactants onto the active region, surface reactions, desorption of products from active region, and diffusion of reactants from the active region. The change in conductivity due to adsorption is described by the equation for conductivity of a semi conductor (1), where conductivity (σ) is equal to the charge of an electron (q) times the carrier concentration (n) times the electron mobility (μ_n) [5].

$$\sigma = qn\mu_n \quad (\text{S}\cdot\text{m}^{-1}) \quad (1)$$

Gas phase diffusion of reactants to the sensor surface is greatly influenced by temperature, with elevated temperatures increasing the rate of diffusion and decreasing transport time to the surface. The reactant gas will begin to adhere to the thin film surface in the process known as adsorption. Adsorption comprises physisorption or chemisorption.

Physisorption or physical adsorption occurs when the adsorbate adheres to the surface through interactions of the van der Waals forces, which are weak intermolecular attractions.

Physisorption is characterized by: low ambient temperature always under the critical temperature of the adsorbate, low enthalpy, and low activation energy.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond. Chemisorption is characterized by: high temperatures, high enthalpy, high activation energy, and an exchange of charge at the adsorbent-adsorbate interface. The chemical bonds that are formed change the carrier concentration through the exchange of charge. In the case of an n -type semiconductor, oxygen adsorbs onto the surface and dissociates, forming O^- or O^{2-} . The O^- extracts a conduction electron from the region near the surface leading to a decrease in conductivity of the sensor.

The decrease in conductivity of the sensor is caused by the chemisorbed oxygen occupying surface states below the fermi level of the metal oxide. This results in a negative surface charge which causes band bending. The band bending results from a depletion of charge carriers, or a decrease in conductivity [6]. As seen in equation 1, fewer conduction electrons yields a lower conductivity. This change in conductivity (σ) can be measured through the reciprocal property of resistivity (ρ), as shown in equation (2), where

$$\sigma = \frac{1}{\rho} \quad (S \cdot m^{-1}). \quad (2)$$

Resistivity can be found by measuring the resistance (R) to an applied current (I) per unit length (l) for a uniform cross section area (A) of the thin film as shown in equation (3).

$$\rho = \frac{RA}{l} \quad (\Omega \cdot m). \quad (3)$$

By applying a current through a uniform specimen of a metal oxide thin film and measuring the voltage, the resistance can be found through Ohm's law, as shown in equation (4) where V is voltage.

$$V = IR \quad (V). \quad (4)$$

Resistance measurements are the basis of measuring most sensor characteristics. Sensor response is determined by the initial and final resistance of a sensor when exposed to a gas.

2.2.3 Sensor Characteristics

Thin film metal oxide gas sensors are characterized by: response, sensitivity, selectivity, response time, range, precision, accuracy, resolution, stability, temperature dependance, and temperature range. The following are specific definitions for general gas sensor characteristics associated with thin film gas sensors:

- *Response* refers to the minimum level of change in detectable sensor output with the minimum level in change of sensor input. More specifically, *Response* is defined as the normalized value of the final output divided by the starting output value, thus *Response* is the final change in the value of sensor resistance (R_s) minus the initial sensor resistance (R_o) over the initial sensor resistance as shown in equation (5).

$$Response = \frac{R_s - R_o}{R_o} \quad (5)$$

- *Sensitivity* is defined as the change in sensor *Response* in relation to a change in gas concentration. *Sensitivity* is the change in sensor *Response* over the change in gas concentration as shown in equation (6).

$$\text{Sensitivity} = \frac{\Delta \text{Sensor response}}{\Delta \text{Gas concentration}} \quad (\text{ppm}^{-1}). \quad (6)$$

- *Selectivity* is the ability of a sensor to be *Sensitive* to an individual gas from a mixture of gasses. Low selectivity is a low sensitivity to an individual gas from a mixture of two or more gasses while high selectivity is a high sensitivity to an individual gas from a mixture of two or more gasses.
- *Response time* (τ) is defined as the time required for a sensor output to change from its initial state to a final settled state value within a tolerance band of the final new value. Response time is often expressed as τ_{90} or τ_{60} meaning the time required to reach 90% or 60% of the final settled state value.
- *Range* is the span of minimum to maximum concentrations that can be measured.
- *Precision* is the degree of reproducibility of measurements at a gas concentration.
- *Accuracy* is the difference from the sensor output and the actual value.
- *Resolution* is the smallest incremental change of gas concentration that can be detected.
- *Stability* is the ability of the sensor to maintain the same gas sensing characteristics over repeated tests.
- *Temperature dependance* is when the output of the sensor is contingent on temperature.
- *Temperature range* is the span of minimum to maximum temperature values the sensor can operate in, while still providing meaningful measurement.

2.2.4 Sensor Testing

Once new gas sensor research devices have been fabricated, testing is required. Testing the gas sensor devices is a critical task for the research effort to determine the response to individual characteristics and the viability of different designs. Proposed testing of new sensors included the factors: response, sensitivity, selectivity, response time, range, precision, accuracy, resolution, stability, temperature dependence, and temperature range for varying concentrations of the target gasses.

Initial sensor designs consisted of IDEs made of a thin film metal layer deposited on a substrate material. A metal oxide thin film is then deposited across the IDE structure. Resistance measurements are taken between the electrodes, with a change in resistance occurring when the metal oxide thin film is exposed to varying concentrations of target gasses. Resistance measurements when coupled with time, temperature, and gas concentration are the basis of all general sensor characteristics. Response, sensitivity, selectivity, response time, range, precision, accuracy, resolution, stability, temperature dependence and temperature range all require accurate resistance measurements. Figure 3 shows a simulated resistance output of a proposed nickel oxide (NiO) sensor device known to be sensitive to H_2 , being tested at a constant concentration and constant flow with varying temperature [7]. The simulated test delivers a constant flow of N_2 with 100 second duration pulses of 2000 ppm H_2 introduced every 200 seconds. The simulated test shows predicted sensor output when H_2 concentration is changed from 0 ppm to 2000 ppm, then back to 0 ppm at temperatures of 400 °C, 500 °C, and 600 °C.

Figure 3. Simulated output of a NiO sensor device sensitive to H₂. The simulated test delivers a constant flow of N₂ with 100 second duration pulses of 2000 ppm H₂ introduced every 200 seconds. The simulated test shows predicted sensor output when H₂ concentration is changed from 0 ppm to 2000 ppm, then back to 0 ppm at temperatures of 400 °C, 500 °C, and 600 °C.

CHAPTER 3

DESIGN CONSIDERATIONS

3.1 Basic Design Considerations

The Test Station design was based upon the goal of testing innovative gas sensors at temperatures greater than 500 °C to determine if the sensors could accurately detect target gasses concentrations. Sensors to be tested came from research on thin film based gas sensor technologies. Initial sensor prototypes were to be made using interdigitated electrodes coated with thin films of metal or ceramic oxides.

Sensitivity and selectivity of thin film sensors depend on the operating temperature as well as the flow rate and composition of the gas [8], [9]. Once a sensor design has been implemented, tests to determine its gas sensing characteristics must be carried out. Testing of new sensors should start with simple tests of individual gasses at constant concentrations and at different temperatures, then expanding to tests that replicate the temperature and combination of gasses of the exhaust stream. These tests must ultimately deliver a variety of components to simulate real world conditions in which the sensors will be used [10], [11]. This means testing should be done at different temperatures with individual gasses or combinations of gasses to characterize the working properties of the new sensor.

Diesel exhaust comprises nitrogen (N_2), water vapor (H_2O), and carbon dioxide (CO_2), with a relatively small concentrations of toxic gasses, such as carbon monoxide (CO), nitrogen oxides

(NO_x), unburnt hydrocarbons, and particulates [12]. Table 1 presents diesel exhaust components under partial and full load conditions [13], [14].

Table 1. Exhaust Products of Diesel Engines.

Exhaust Product	Partial Load	Full Load
Nitrogen	75%	68%
Oxygen	15%	0.8%
Carbon dioxide	7%	21%
Water vapor	2.6%	8.5%
Carbon monoxide	430 ppm	7000 ppm
Nitrogen oxides	340 ppm	1000 ppm
Hydrocarbons	50 ppm	1200 ppm
Hydrogen sulfide	40 ppm	800 ppm
Sulfates	40 ppm	700 ppm
Aldehydes	10 ppm	150 ppm

Gas sensor test stations often use volumetric flow control to regulate the flow rate and concentration of gas to which the sensor is exposed [15], [16]. The collection of data showing electrical changes to the sensor is also part of most test apparatuses [17], [18]. The ability to maintain a precise temperature is another feature used to investigate new sensor designs [19]. Moisture content of the test gas is also a desired feature [20], [21].

Test Station material and component choices were restricted by the planned use of aggressive gasses as well as the desire to minimize out-gassing. Thus, minimum requirements for a new gas sensor Test Station would include: variable gas concentration and flow, sample heating, electrical

data acquisition, and vacuum grade components for wetted hardware [22].

3.2 Gas Composition and Flow Control

The general process flow, shown in Figure 4, commences with a metered flow of test gas diluted by a metered flow of carrier gas to reach the desired concentration and volumetric flow. The test gas can be delivered with or without humidity by routing through an H₂O bubbler. The diluted gas combination is introduced to the test chamber, in which the sensor being tested is exposed to the gas flow. The test gas then exits the chamber. Electrical resistivity measurements are collected as a function of time from the sensor prototype during the entire test.

Test gasses and their concentrations were chosen to simulate diesel engine and gas turbine exhaust streams, with the addition of NH₃ a gas used in emission controls [23]. These concentrations are shown in Table 2. The *response time* for the Test Station is the time required for the gas to reach the chamber once the flow has been started. The *turnover time* is the amount of time required for supplied gas flow to replace the gas in the test chamber one time [24].

A gas sensor response time as short as possible was desired, with the goal of having response times on the order of seconds or 10s of seconds [25]. Typical gas sensor response times (τ_{90}) are less than one minute [26], [27]. Thus, a *gas response time* of less than 5 seconds and a *gas turnover time* of 10 seconds were chosen to avoid significant effect on the measured response [28], [29].

Figure 4. Preliminary process flow design. Test gas (humid or dry) is mixed with a carrier gas to achieve desired concentration, then flows through the test chamber. Data collection occurs simultaneously.

Table 2. Test Gas and Concentration.

Gas	Concentration
Water vapor	0 - 100%
Hydrogen	1 - 20000 ppm
Oxygen	1 - 20000 ppm
Carbon dioxide	1 - 5000 ppm
Carbon monoxide	1 - 3000 ppm
Nitrogen oxides	1 - 800 ppm
Ammonia	1 - 800 ppm
Methane	1 - 500 ppm
Sulphur oxides	1 - 350 ppm

3.3 Heater Considerations

Temperature is an important operating variable for gas sensors. Gas sensitive thin films, often exhibit changes in sensitivity, selectivity, etc. at different temperatures [30]; thus, testing across a wide range of temperatures is important. The sample heater should enable investigating the stability of sensors at high temperatures in aggressive gasses. Also of concern are resistance variations due to temperature fluctuations. As a result, the sample heater in the Test Station must be able to maintain a uniform and stable temperature across its surface [31], [32].

Two common methods to control the temperature of gas sensitive film include integrating a resistive micro-hotplate device [33] or heating the sensor externally. External heating is generally accomplished through the use of a furnace or a heated chuck. Integrated micro-hotplates can allow rapid and exact heating of the sensor, but require this structure be characterized before experimental sensors can be tested [34].

A heated chuck has the advantage of helping to reduce the test chamber volume, thus decreasing the *gas turnover time*. Chucks are often heated by using cartridge type heaters. A significant disadvantage of cartridge heaters is the upper temperature limitation of less than 750 °C. A furnace has the advantages of temperatures above 1000 °C, and more uniform heating. This is countered by the relative large chamber size of most furnaces as compared to heated chuck designs. This larger furnace chamber size would required fabrication of a specialized inner furnace chamber increasing the cost of a furnace as compared to a heated chuck.

A heated chuck design was chosen for the initial Test Station design primarily because it was less expensive than a furnace design, and secondarily because a small test chamber size outweighed the desire to reach temperatures greater than 650 °C. A significant concern with a heated chuck

design was temperature uniformity across the chuck. Thermal simulations of the heated chuck were to be used to determine the best design to maximize temperature uniformity.

3.4 Electrical Data Acquisition Considerations

Thin film gas sensors can change resistivity when exposed to concentrations of certain gasses. Measurement of the resistivity change is used to calculate most sensor characteristics. Electrical connections were needed to collect data and measure the changes in electrical properties of the thin film gas sensors with temperature and gas exposure. Common methods to make electrical connections include traces and bond pads on the sensor with the sensor mounted in a header (e.g., TO8) with wire bonded connections. A card-edge type connector could be used with all sensor designs, but would require that all sensor designs incorporate the dimensions of the card-edge connector.

For sensor prototypes, packaging sensors with TO8 headers may not be efficient as many designs will not be fully functional. The use of a card-edge type of connection restricts the sensor design to the specific dimensions of the card-edge connector. Greater flexibility and the ability to make electrical connections to a variety of sensor prototypes was needed which would be a challenge for card-edge connections [35].

Additionally, a system of probe needles controlled by micromanipulators was determined to be suitable for making contact to bond pads on the sensors. This design could use commercial off-the-shelf components, reducing cost. Probe needles have an additional advantage of being inexpensive and replaceable reducing variability caused by corrosion or surface contaminants.

3.5 Design Requirements

All wetted surfaces in contact with the test gas were chosen to be vacuum compatible to ensure that no out-gassing or introduction of impurities occurred aiding stability and longevity of the Test Station. The test chamber was designed with a low volume to achieve a *gas response time* of less than 5 seconds and a *gas turnover time* of less than 10 seconds. The cross sensitivity or selectivity needed to be measured which required introducing multiple gasses at the same time. The test apparatus was designed to accommodate a total of 4 test gasses. The system was required to supply 2 carrier gasses such as N₂ or synthetic air to allow for testing sensors with dilute concentration of test gasses in a realistic ambient. To achieve a variable concentration of the test gas, the flow was required to be metered to vary the concentration by 1 order of magnitude.

The heated chuck was required to maintain temperature fluctuation of less than ± 1 °C. This level of control is needed because resistivity and gas sensor characteristics are typically strong functions of the operating temperature. Electrical connections to the prototype sensors were needed to connect the sensors for resistivity tests. A summary of the design requirements is shown in Table 3.

Table 3. Design Requirements Summary.

1	All wetted components are vacuum compatible
2	Small test chamber volume - <i>gas turnover time</i> of less than 10 seconds
3	Accommodate 4 test gasses and 2 carrier gasses
4	Control gas concentration across 1 order of magnitude
5	Ability to heat sensor to 650 °C
6	Temperature accuracy of ± 1 °C

7	Electrical connections to sensors under test
8	Electrical resistance measurements from $1\text{m}\Omega$ to $100\text{M}\Omega$
9	Computer control of subsystems
10	Data logging of temperature, test gas flow, and sample resistivity

CHAPTER 4

TEST STATION DESIGN

4.1 Overall Design

Industry standards for vacuum grade components mandate the use of stainless steel. All piping was specified to be 1/4 inch 316 stainless steel with all wetted surfaces to be acid washed or electro-polished. The project requirements presented a particular design challenge: the test chamber needed to be sufficiently small to allow a fast gas turnover rate, yet large enough to house the adjustable electrical connectors and a heated chuck.

The Test Station design was to be a sealed stainless steel chamber containing a heater and probe connections. Solidworks[™] CAD software [36] was chosen as the tool to design the test chamber. Because of the ability to model critical fits among the various parts, the use of CAD tools was required for keeping chamber volume to a minimum. Figure 5 outlines the test chamber design with the planned location for components.

Figure 5. CAD design of the test chamber. The test chamber has an inner diameter of 7.6 cm and is 3.81 cm tall. Test chamber mounts to top of test chamber base.

The chamber volume needed to be small enough to allow a *gas turnover time* of less than 10 seconds using chosen gas flow control components (see section 4.2). Gas flow through the chamber and process piping needed to be at sufficient volumes to purge the chamber at the specified rate, low enough to minimize the use of test and carrier gasses, and to avoid turbulence effects and pressure gradients. The chamber was designed to use 1/4 NPT fittings for gas inlet and gas outlet ports. The ports were located on opposite sides of the chamber to maximize *gas turnover time*. Additionally, the chamber needed 2 electrical feedthroughs: one for the 8 probe needles and another for heater power and thermocouple connections. Considering the effect of chamber size on user operability

yielded an optimum design of a chamber 7.6 cm in diameter by 3.81 cm tall. This resulted in a designed test chamber volume of 174 cm³. The internal volume was further reduced by the heated chuck and the electrical probes to a net volume of 140 cm³. The chamber was designed to be easily removed from the chamber base to allow access to the heated chuck and the electrical probes.

4.2 Gas Flow Design

To achieve a large range of gas concentrations and flow rates for test gasses, the gas flow requires a mixture of one or more test gasses diluted in a carrier gas. Mass Flow Controllers (MFCs) were chosen for their ability to accurately and repeatedly control gas flow. MFCs use the heat capacity of a gas to measure flow rates and therefore are somewhat independent of temperature and pressure. Typical MFCs create a temperature difference between the two resistive elements. As gas flows through the MFC, cooling occurs. This change in temperature is measured as resistance change due to the temperature differential. This electrical signal is then correlated to gas flow based on known gas heat capacities. MFCs accurately measure gas flow rate from 3 SCCM to 30 SLM, thus allowing a wide range of test gas concentrations.

One drawback of MFCs is their inability to effect a leak proof seal when flow is set to zero. Electro-servo valves were planned as main flow control valves to assure positive open and closed states. For maximum safety, normally closed (NC) valves were specified so that all gas flow would cease in the event of a power failure or emergency stop. Figure 6 shows the gas flow design including all valves and MFCs.

Figure 6. Gas flow design. Individual test gasses are controlled by solenoid valves (SV) 0 to 4 with SV5 used for purging. Carrier gasses are controlled by SV6 and SV7.

Given the estimated chamber volume of 140 cm^3 (section 4.1), a mass flow controller rated to 6000 SCCM, predicts an ideal *gas response time* of 1.40 seconds, calculated by dividing flow rate by chamber volume. Convection, turbulence, gas mixing and obstructions all influence the turnover rate. The design eliminates obstructions in the flow over the sample being tested, but convection and turbulence will reduce *gas turnover time* by a significant amount. This effect was estimated to increase turnover rate time by no more than 25%, yielding a minimum gas turnover rate of less than 2 seconds. A maximum flow rate is calculated by using the lowest predicted flow rate of 1200 SCCM. Minimum flow *gas turnover time* is predicted to be 7.5 seconds with convection and turbulence increasing this time to approximately 10 seconds.

4.3 Heater Design

The heated chuck design utilized a metal disk with cartridge-type heaters. Cartridge heaters are cylindrical, metal encased resistive heaters. The 6 cartridge heaters at 50 Watts each (300 Watts) were installed inside the disk creating a heated chuck.

The heated chuck was constructed from stainless steel to resist corrosion and have good thermal conductivity. Most metals with high thermal conductivity such as copper and its alloys did not meet the design requirement for chemical inertness required due to the use of oxidizing target gasses. Corrosion resistant metals such as Hastelloy and Inconel have good thermal conductivity and low oxidation rates, but are difficult to machine due to their high strength, work-hardening, and "gumminess" especially considering the desire to machine parallel 1/4" holes with wall thicknesses between holes of less than 0.005". Stainless steel was ultimately selected because it provides a good trade-off between cost, thermal conductivity, machinability, and is fairly inert. Once stainless steel

was selected, Grade 316 was considered to be the most appropriate grade because it contains molybdenum, which is used extensively in harsh environments and the medical field; however, it is susceptible to carbide precipitation where carbon in solution precipitates at temperatures above 600 °C [37]. Carbide precipitation is aggravated by water vapor, and water vapor is one of the target gasses.

Grade 316L stainless steel has a lower carbon content than 316 and is better suited for use above 600 °C, especially when exposed to water vapor as it is less susceptible to corrosion caused by carbide precipitation. The lower carbon content of grade 316L steel is easier to machine when compared to 316 stainless steel. Grade 316L stainless steel was chosen as the heater material in the Test Station because it had the best combination of thermal conductivity, corrosion resistance, and machinability. General mechanical, thermal, and electrical properties of 316, 316L, Hastelloy, and Inconel are presented in Table 4, Table 5, and Table 6, respectively. The oxidation rates for these materials are given in Table 6. Copper is included as a reference as a material with excellent thermal conductivity but has a high rate of oxidation and chemically reacts with several proposed test gasses.

Table 4. Heater Material Mechanical Properties.

Metal	Hardness Brinell [HB]	Tensile Strength [MPa]	Density [Kg/m ³]	Young's Modulus [GPa]
316	149	550	8000	193
316 L	149	515	8000	193
Hastelloy C 22	201	101	8690	206
Inconel 617	172	734	8360	211
Copper (OFC)	49	200	8940	125

Table 5. Heater Material Thermal Properties [38].

Metal	Thermal Conductivity 100 °C [W/m·K]	Thermal Conductivity 500 °C [W/m·K]	Thermal Expansion Co- eff 100 °C [μm/m/°C]	Thermal Expansion Co- eff 500 °C [μm/m/°C]
316	16.3	21.5	16.2	17.5
316 L	16.3	21.5	16.2	17.5
Hastelloy C 22	11.1	19.5	12	13.4
Inconel 617	14.7	21.3	11.6	14.7
Copper (OFC)	385	400	17.3	20.2

Table 6. Heater Material Electrical Resistivity and Oxidation Rate [39].

Metal	Electrical Resistivity [μΩ.cm]	Oxidation Rate 300 °C [μm/100 hrs]
316	78	0.2
316 L	72	0.120
Hastelloy C 22	12.3	0.03
Inconel 617	73.6	0.01
Copper (OFC)	1.7	30

CAD design of the heated chuck with respect to the test chamber was undertaken to minimize the size of the heater. Using the chamber dimensions of 7.62 cm diameter by 3.81 cm high the heated chuck was designed to be 4.45 cm in diameter and 1.27 cm thick. Figure 7 presents a

rendering of the heated chuck design located within the test chamber. The top of the chamber is normally closed but is shown open for modeling purposes.

Figure 7. Rendering of heated chuck inside the test chamber. The heated chuck is 4.45 cm in diameter and 1.27 cm thick. The heated chuck is elevated off the base by 0.3 cm using ceramic beads. The chamber dimensions are 7.62 cm inside diameter by 3.81 cm high. One micromanipulator is shown attached to a mounting post. Electrical and gas feedthrough holes are also shown. The top of the chamber is normally sealed but is shown open for modeling.

4.3.1 Temperature Control

Specifications for the Test Station required accurate temperature control in the upper operating range of the heating elements. A temperature controller using the proportional integral derivative algorithm (PID) was chosen because the PID feedback type of control is the most commonly used with a reputation of consistency and reliability.

The proportional (P) part of the PID control alters the input by the same proportion that the output is in error by calculating the reaction to the error between the input and output. The addition of integral feedback control increases accuracy by calculating the integral or rate of change of the output versus the input.

The Integral (I) part of the PID control calculates the new reaction based on the sum of the most recent errors. For maximum accuracy, derivative control is added to proportional and integral allowing for varying changes to the reaction based on oscillation [40].

The derivative (D) part of the PID control calculates the reaction to the error change rate and changes the output proportional to the change in process error over time multiplied by the derivative gain. The P, I, and D outputs are summed to produce the controller output, thus a PID controller maintains a desired set point by altering the responsiveness to the error, the over shoot, and the amount of oscillation. A block diagram of the PID controller loop is shown in Figure 8.

Figure 8. Schematic shows a PID controller loop diagram.

The PID controller drives a solid-state relay (SSR), and this relay makes or breaks the power to the heating elements installed in the heated chuck. The controller uses a thermocouple installed in the heated chuck for temperature feedback. The PID controller provides a variable duty-cycle in accordance to the control calculations that regulates the power to the heated chuck to achieve the desired temperature. Figure 9 shows the PID controller and heated chuck electrical block diagram.

Figure 9. Diagram shows PID controller and heated chuck electrical block diagram. The PID controller receives chuck temperature feedback from the thermocouple, altering the duty cycle of the SSR and thus power to the cartridge heaters to achieve the desired temperature.

4.3.2 Thermal Modeling

A significant concern with the heated chuck design was temperature variability across the surface of the heater. Grade 316L stainless steel has low thermal conductivity compared to metals such as copper. Modeling the thermal characteristics of the heated chuck was carried out as part of the design process. The heater was modeled using finite element analysis in Ansys[™] simulation software. The heater was modeled as a 4.45 cm diameter 1.27 cm thick stainless steel disk. Six holes were extruded through the chuck where the heater cartridges were to be installed. The entire surface of each hole was selected as the heat generation surface representing the active heater cartridge. A value up to 50 Watts to the surface of each hole was used as the input quantity of heat generated by each cartridge heater for a to. A basic convective model was chosen with a heat transfer gradient from room temperature to maximum temperature. In addition to the convective model, a conduction model was used air filled space around the heated chuck and the test chamber surface modeled as

stainless steel at room temperature. The modeling software showed a fairly even heat distribution across the heated chuck. The software predicted a maximum temperature variation of 3 °C across the heated chuck. The hottest area of the heated chuck is centrally located with the temperature decreasing towards the edge of the chuck.

Figure 10 shows a graphical representation of the thermal modeling as predicted by finite element analysis. Each color change represents 3 °C with the hottest area of 800 °C represented by the central purple color. Prior tests showed excessive thermal conduction occurring from the heated chuck to the base. Elevating the heated chuck by 0.3 cm off the base created an insulating layer of air that minimized these thermal conduction losses. Three 0.3 cm ceramic spacers were planned to elevate the heated chuck.

Figure 10. Figure shows finite element analysis software model of heater. The 6 holes are where the cartridge heaters are located. Each hole surface was selected as a heat generation surface of 50 Watts. Centrally located purple color represents 800 °C. Each color change represents 3.2 °C.

4.4 Electrical Data Acquisition

4.4.1 Micromanipulators and Electrical Probes

Micromanipulators were chosen to make contact to sensor die as they provide more flexibility than header based designs. Micromanipulators can accommodate different sensor designs as well as minimizing restrictions on sensor sizing. They do have several significant disadvantages:

difficulty in connecting to small die sizes or small bond pads, oxidation of the probe needles when exposed to corrosive gasses, and varying contact resistance due to nonuniform contact pressure.

Off-the-shelf electrical probes were required to connect to the contact pads of each sensor prototype to provide for these electrical measurements. The maximum size of each sensor was specified to be 15 mm square and the contact pads on the sensors were less than 1.5 mm square. The addition of micromanipulators allows for accurate placement of the probes on the contact pads.

Micromanipulator based probe stations, accurate to less than one micron, are common in industry but are rarely compatible with temperatures in excess of 400 °C. To resolve this limitation, existing off-the-shelf micromanipulator designs were modified, replacing low temperature components (nylon or Teflon gears) with high temperature versions (stainless steel). Designs for custom fabricated 3 axis micromanipulators are shown in Figure 11 and Figure 12.

The stainless steel micromanipulators were to be electrically isolated from the test chamber base via a ceramic plate. Although this design was considered to be the best available, it also was the most expensive by an order of magnitude, and budgetary constraints eliminated this design. A second micromanipulator design used off-the-shelf swivel clamps, Figure 13 and Figure 14, attached a probe needle clamped to a ceramic post. This second design is shown in Figure 15 and Figure 16.

To electrically isolate the probe needles, the micromanipulators were to be mounted on ceramic posts. The swivel clamps with post design limits total number of probe connections to a maximum of 8 probes for a total of 4 channels.

Figure 11. Diagram shows an expanded view of stainless steel 3 axis micromanipulator structure.

Figure 12. Diagram shows an assembled view of stainless steel micromanipulator structure.

Figure 13. Photograph of commercial off-the-shelf stainless steel swivel clamp.

Figure 14. Photograph of probe needle mounted in commercial swivel clamp.

Figure 15. Diagram shows a side view of swivel clamp type micromanipulator attached to a ceramic post.

Figure 16. Diagram shows top view of swivel clamp type micromanipulator attached to a ceramic post.

A third generation of micromanipulators consisted of a probe needle mechanically bonded to a micromanipulator arm with ceramic adhesive. The ceramic adhesive electrically isolates the probe needles from the metal structure while firmly securing the probe needle. This design mounts clamp type micromanipulators to metal posts. The clamp type micromanipulator design was chosen as the best of the 3 designs due to costs of parts and ease of manufacturing.

The electrical probes connect the device being tested to the data acquisition hardware. The probe electrodes were connected to terminal blocks for the ease of future modifications.

4.4.2 Data Acquisition

Measurement of the sensors' resistivity was to be accomplished with a digital multi-meter (DMM). Due to the desire to sample multiple sensors simultaneously, a multi channel Keithley model 2700 DMM was selected to fulfill these measurements requirements. The data from the DMM needed to be recorded in real time and be stored for analysis. The data acquisition and recording as well as real time analysis was to be accomplished by the use of an HMI. A general schematic of the electrical measurement and data acquisition is shown in Figure 17. The Keithley model 2700 is a good all around meter for resistance measurements with a voltage range of 100 mV to 100 V and a current range of 20 mA to 3 A, giving a resistance range of 10 m Ω to 100 M Ω . To conduct measurements outside the range of the 2700, a Keithley model 2400 was added to channel 1. The Keithley model 2400's voltage range is 1 μ V to 210 V and its current range is 10 pA to 1 A, giving a resistance range of 1 $\mu\Omega$ to 211 M Ω and as a result has a wider range of measurements.

Figure 17. Drawing shows electrical measurement and data acquisition schematic. Data from channel 1 is read by either the DMM or source meter and data from channel 2 - 4 is read by the multi-channel DMM only. The PC controls the DMM and source meter and records the data for later analysis.

4.4.3 Human Machine Interface Control

Use of an HMI allows the user to assess the state of the system and load specific commands. HMI also allows for the continuous recording of input and measured parameters. The HMI communicates with all connected devices using the communication protocol of each individual device, thus allowing for control of the entire system from a single personal computer (PC). National Instruments brand LabVIEW Software [41] was used to program the HMI specifically because of its built in driver compatible with many scientific instruments and components. LabVIEW incorporates good routines for acquiring, presenting, and storing data and enjoys wide

acceptance in the industry and for its user friendly graphical user interface (GUI). The task of LabVIEW HMI was to make the test process safe and repeatable and to automate repetitive or long duration tasks.

The HMI written in LabVIEW controls:

- DMM - Acquires resistance data, time stamps and logs data.
- Source meter - Sets current and voltage levels, acquires current and voltage data, time stamps and logs data.
- MFCs - Controls gas flow and acquires flow rate, time stamps and logs data.
- Solenoid valves - Actuates the valves and records time stamped state of valve.
- PID controller - Sets temperature set point, acquires temperature data, time stamps and logs data.

CHAPTER 5

TEST STATION AS BUILT

5.1 Systems and Subsystems

The subsystems of the Test Station system include: the test chamber, the gas flow controls, the heater controls, the electrical data acquisition, computer/HMI, and the cooling system. The Test Station was constructed using a 112 cm tall ,46 cm rack mount cabinet on casters, an accompanying work table, and a mobile gas cart. All subsystems are contained in the main rack mount cabinet. The entire Test Station can be easily moved by a single individual. The completed Test Station is pictured in Figure 18.

Figure 18. Rack mounted Test Station is shown. The test chamber is on top of the main cabinet. The main cabinet on left houses: the gas flow controls, the heater controls, and the electrical controls.

5.2 Test Chamber

The test chamber was constructed of 304 stainless steel and consisted of a base with a removable chamber. The base contains all gas, electrical, and water cooling feedthroughs, and the supports for the electrical probes. The removable chamber is cylindrical shaped with interior dimensions of 7.62 cm in diameter by 3.81 cm tall and a wall thickness of 1.27 cm, giving a total chamber volume of 174 cm³. The interior volume is further reduced by the heated chuck with

cartridge heaters, and the micromanipulators with probes consuming an additional 26 cm³ and 16 cm³ respectively, resulting in a chamber volume of less than 132 cm³. The test chamber exterior is pictured in Figure 19, with the interior shown in Figure 20.

5.3 Gas Flow System

The gas flow supplied to the chamber is a mixture of up to 4 test gasses diluted with a carrier gas. The gas control system uses Celerity model 8101C mass flow controllers (MFCs) to deliver an exact concentration of test gas at a specific flow rate [42]. The test gas MFCs are rated for a maximum flow of 750 SCCM, whereas the carrier gas MFCs are rated for a maximum flow of 6,000 SCCM. Thus, maximum flow through the Test Station is 6750 SCCM. For positive on and off control of the gas flow, electro-servo valves were used. The valves are DC powered and controlled by the HMI. The default condition is normally closed (NC). Thus, if the power fails or if the emergency shut-off (ESO) is activated, all gas flow ceases. The Test Station incorporates bulkhead fittings for gas flow connections to the case of the Test Station. These bulkhead fittings were internally connected to the individual gas lines connected to each MFC. This allowed the MFCs to be placed closer to the test chamber, minimizing the *gas response time*. Figure 21 is a photograph of the mounting plane mechanical layout of control valves, MFCs, DC power supplies, electrical termination blocks, and the gas input and output locations. A piping diagram showing gas flow is shown in Figure 22. The gas flow may also be re-directed to pass through the H₂O bubbler which humidifies the gas flow.

Figure 19. Photograph shows test chamber exterior view.

Figure 20. Photograph shows test chamber interior view.

Figure 21. Photograph shows Test Station gas flow mounting back plane. This mounting plane shows the proximity of gas flow control valves and MFCs.

Also shown are the DC power supplies and electrical termination blocks.

Figure 22. Piping diagram showing process flow from bottom to top, starting at gas source
 Process flow continues through individual MFCs and solenoid control valves to the
 mixing manifold. Test gas flows can be redirected through an H₂O bubbler.
 Test gas and carrier gas mix is then introduced into test chamber.

The Test Station was optimized for gas flow of 750 SCCM to 6,000 SCCM with maximum concentration variation occurring at a total flow rate of 750 SCCM. The system can vary the concentration of the test gas source (e.g., cylinder) as calculated from (5). Increasing or decreasing the total flow rate reduces the available concentration range.

$$Concentration(ppm) = \frac{TestGas(SCCM)}{CarrierGas + TestGas(SCCM)} Tank(ppm) \quad (5)$$

The concentration range for a constant flow rate can be varied from 0% to 100% while maintaining a constant flow rate of up to 750 SCCM. For a varied concentration/constant flow rate the flow rate can be increased above 750 SCCM with a reduction in concentration. The flow rate range for a constant concentration can be varied from 0 to 6750 SCCM while maintaining a constant concentration of 11% or less of source test gas. The range of concentration versus total flow rate is shown in Figure 23. The shaded area shows the available range of use.

Figure 23. Gas Flow Rates versus Concentration range of use (denoted by the blue area). Concentration is defined as a percentage of source gas concentration. The concentration range for a flow rate up to 750 SCCM, can be varied from 0% to 100% of source. (The flow rate for a concentration up to 11%, can be varied from 0 to 6750 SCCM.)

Given an effective chamber volume of 132 cm^3 , and maximum flow at 6750 SCCM (100 cm^3/sec) a predicted ideal *gas response time* of less than 2 seconds is calculated using equation (6).

$$\frac{132 \text{ cm}^3}{100 \text{ cm}^3/\text{sec}} = 1.32 \text{ sec} \quad (6)$$

At a total flow rate of 5800 SCCM, the *gas response time* for the chamber was 1.5 seconds as confirmed by using measurements from commercial sensors placed inside the test chamber and

exposed to actual gas flow [43], [44]. Actual measurements using a commercial gas sensor downstream of the chamber confirm that the chamber does achieve a *gas response time* of 1.8 s to 5 s (depending on gas flow). The *gas response time* was determined by measuring time it took a test gas reached a concentration of more than 10% of test concentration. Figure 24 shows the response Umwelt Sensor Technik (UST) model 5000 commercial NO_x sensor. The sensor was exposed to a constant concentration of 100 ppm NO_x, while total flow of 750 SCCM to 5800 SCCM was used. The sensor showed little variance in the *gas response time* across the range of flow. Figure 25 shows a zoomed in view of the *gas response time*. The commercial sensors could not be exposed to the elevated temperature so all gas response time tests were done at room temperature. The high temperatures normally used for tests would undoubtedly alter the gas flow through the test chamber via convection effects and may increase the *gas response time*.

The available range of concentration versus flow rate for all target gasses is shown in Figure 26 and Figure 27. Figure 26 shows high concentration (3,000 to 20,000 ppm) gasses with Figure 27 showing the low concentration (300 to 800 ppm) gasses.

Figure 24. Sensor response measurements using Umwelt Sensor Technik (UST) model 5000 commercial NO_x sensor. The sensor was exposed to NO_x at a concentration of 100 ppm at both 750 SCCM and 5800 SCCM.

Figure 25. Zoomed in view of Figure 24, sensor response using UST 5000 NO_x sensor. Resistance is shown to accentuate the difference between the gas flow.

Figure 26. Plot of gasses available and range of concentrations for low concentration (300 to 800 ppm) gasses.

Figure 27. Plot of gasses available and range of concentrations for high concentration (3,000 to 20,000 ppm) gasses.

5.4 Heater System

5.4.1 Heated Chuck

The heated chuck was made from 316L stainless steel machined into a disk, 4.45 cm in diameter and 1.27 cm tall. Holes for cartridge heater were machined through the center of the chuck with an additional hole drilled for the thermocouple. The initial positioning of the holes for the cartridge heaters was based on thermal modeling of the heated chuck. The actual position was modified to its current design after building the initial design. The actual design used is a byproduct of thermal modeling and trial and error. A picture of the chuck is presented in Figure 28 showing seven parallel holes, six for cartridge heaters and one for the thermocouple. The thermocouple hole is the lower central hole.

5.4.2 Heating Elements and Thermocouple

The heating elements used were six 50 W, 110 VAC, Wattlow resistive cartridge heaters sheathed in Inconel [45]. The cartridge heaters were 0.64 cm in diameter and were mounted in parallel through the middle of the chuck. The heated chuck also used a K-type thermocouple located inside the disk. The thermocouple output was acquired by a PID based temperature controller and used to control the feedback loop. A single cartridge heater and thermocouple are shown in Figure 29. The heated chuck with 4 heaters and thermocouple partially installed is shown in Figure 30.

Figure 28. 316L Stainless steel chuck 4.45 cm in diameter and 1.27 cm tall. Cartridge heaters mount in six 0.64 cm holes with thermocouple mounted in the lower central hole.

Figure 29. Inconel sheathed cartridge heater (bottom) and K-type thermocouple (top).

Figure 30. Heated chuck with heaters (4 of 6 left side) and thermocouple (right side) partially installed.

5.4.3 PID Controller

The PID controller is a Watlow model SD and generates a 0 to 6 VDC output controlling a 30 SSR. The SSR in turn regulates the time 110 VAC power is supplied to the cartridge heaters, thus varying the duty cycle to control the chuck temperature. The PID controller is accurate to 0.01 °C and has a minimum response time of 5 ms. The PID controller communicates with the HMI via the Modbus communication protocol.

Table 7 presents characteristics of the heater system. Figure 31 shows the relationship between heater temperature and power applied to all six 50 W heating elements.

Table 7. Heater System Properties.

Temperature		
Variable	500 °C	650 °C
Response time (from 20 °C)	150 seconds	180 seconds
Temperature resolution	± 0.5 °C	± 1.5 °C
Power required peak	142 Watts	220 Watts

Figure 31. Heated chuck temperature versus peak power applied for six 50 W heaters.

5.5 Electrical Data Acquisition System

The electrical data acquisition system consists of micromanipulators with electrical probes, the HMI, and data acquisition components (e.g., DMM). The current design of the Test Station provides for using up to 8 electrical probes for a total of 4 channels. The sensor's resistivity is measured using a Keithley model 2700 DMM with a 40 channel differential I/O expansion card. The I/O card provides accurate resistivity measurement for multiple channels allowing multiple sensors to be sampled simultaneously. As specified, a Keithley model 2400 source meter is installed on a single channel for current and voltage measurements beyond the range of the DMM. One set of probes is connected to both the DMM and the source meter via a relay allowing either meter to measure that channel. The Keithley model 2700 has a voltage range of 100 mV to 100 V and a current range of 20 mA to 3 A, yielding a resistance range of 10 m Ω to 100 M Ω . To conduct measurements outside the range of the 2700, a Keithley model 2400 was added to channel 1. The Keithley model 2400's voltage range is 1 μ V to 210 V and its current range is 10 pA to 1 A, giving a resistance range of 1 $\mu\Omega$ to 211 M Ω . A low impedance relay switches the probe needles of channel 1 to either the Keithley 2400 or the Keithley 2700 via a front panel switch.

5.5.1 Probe Connections

The electrical probes and associated micromanipulators used the third design of micromanipulators consisting of a probe needle mechanically bonded to a micromanipulator arm with ceramic adhesive. The ceramic adhesive electrically isolates the probe needles from the metal structure while firmly securing the probe needle, Figure 32. This design uses custom made clamp type micromanipulators as shown in Figure 33 and Figure 34. A barrel-type electrical connector,

shown in Figure 35, is used to connect the probe needle to a wire lead running to the measurement DMM. This barrel connector was an improvement upon crimp type connectors as the latter would lose electrical connectivity due to repeated thermal cycling from the different type of materials of the probe needle and the crimp connector, as well as corrosion from exposure to aggressive gasses. Stainless steel wires were used to connect the probe needles of the electrical feed through connections through the base of the test chamber.

Figure 32. Photograph shows probe assembly before and after ceramic adhesive. Top shows tungsten needle and stainless steel shaft. Bottom shows ceramic adhesive bonding the needle and shaft creating an electrically isolated probe.

Figure 33. Photograph shows custom swivel clamp components.

Figure 34. Photograph shows micromanipulator with probe assembly, side and top views.

Figure 35. Photograph of a micromanipulator and probe assembly with “barrel-type” connector attached.

The micromanipulators incorporate 3 axes of adjustability. Using the cylindrical coordinates (ρ, ϕ, z) , the probe needle arm sweeps out a circular arc (ϕ) 72 degrees wide, spanning a 2.0 cm wide path across the surface of the heated chuck. The probe needle arm extends out in the radial direction (ρ) 2.0 cm with 1.0 cm vertical travel in the z direction. Figure 36 illustrates the area 2 probes can contact when operated as a single channel. The Test Station can accommodate a variety of sample dimensions due to the adjustability of the micromanipulators. Figure 37 shows a 7.5 mm² sample ready for testing.

Figure 36. Illustration of heated chuck showing probe needle contact area for a single channel. The yellow area denotes probe 1 range of movement, blue area denotes probe 2 range of movement, and the green area is the range covered by both probes. The sample size is 7.5 mm^2 .

Figure 37. Photograph showing heated chuck a with 7.5 mm² sample. Two probes are connected to the sample in preparation for a gas sensor test.

5.5.2 Human Machine Interface

The HMI is a custom written LabVIEW program that controls the Test Station hardware and collects data from the DMM. LabVIEW was selected because of its relatively easy and robust ability to interface with measurement systems and process controls and its graphical user interface (GUI). The HMI was designed to make the test process safe, repeatable, and to automate repetitive or long experiments. The HMI also allows for the continuous recording of input and measured parameters. Figure 38 presents a screen shot of the HMI control screens.

Figure 38. Screen shot of HMI gas flow control and data acquisition modules.

5.5.3 Data Acquisition

Optimizing the gas sensitivity of the thin film layers requires the investigation of relationships between deposition conditions and the gas sensing characteristic. Sample sensors were placed on the heated chuck and heated to the operating temperature, the maximum temperature which was 650 °C, while continually measuring their resistivity. During the experiment, a known test gas concentration was to be introduced. Once a specific gas sensor sample was placed into the test chamber, the entire experiment was automated by computer control. The system generates a real time graph of test data and also saves the data to an ASCII file. The HMI helped maintain safety, repeatability, and speed as well automating data collection. Throughout the entire experiment,

electrical resistivity, gas flow and concentration, as well as the operating temperature were logged.

This data was later compiled into a graphical representation as shown in Figure 39.

Figure 39. Gas sensor response of an indium oxide sample exposed to 15 ppm NO_x at temperatures from 400 °C to 650 °C. This plot shows the initial 60 seconds of sensor response.

5.6 System Measurement

5.6.1 System Specifications

The temperatures may be varied from room temperature to 700 °C with an accuracy of ± 0.5 °C at 500 °C, and ± 1 °C at 650 °C and a response time of 8 seconds. The electrical resistance measurements take a minimum of 10 ms and have a range from 100 m Ω to 200 M Ω . Gas concentration range, for a flow rate up to 750 SCCM, can be varied from 0% to 100% of source gas. The flow rate for a concentration up to 11%, can be varied from 0 to 6750 SCCM. System specifications are summarized in Table 9.

Table 9. Table of System Specifications

Variable	Value
Heated chuck temperature range	20 °C - 700 °C
Data acquisition channels	4
Resistance measurement - single channel	1 $\mu\Omega$ - 211 M Ω
Resistance measurement - multi channel	10m Ω - 100 M Ω
Voltage measurement - single channel	1 μ V - 210 V
Voltage measurement - multi channel	100 mV - 100 V
Current measurement - single channel	10 pA - 1 A
Current measurement - multi channel	20 μ A - 3 A
Data acquisition rate - single channel	10 msec
Data acquisition rate - multi channel	550 msec/channel
Gas concentration range	0% - 100% of source
Gas flow range	0 SCCM - 6750 SCCM

Number of test gasses	4
Number of carrier gasses	2
Relative humidity of test gas	0% - 100% (at 90 °C)

5.6.2 System Influence on Test

The system introduces $4.8\ \Omega$ of resistance to the measurement. This is due principally to the stainless steel wires used to connect the system to the probes inside the test chamber.

Thermal noise is introduced at elevated temperatures. This may be due to a temperature gradient that exists between the micromanipulators and the heated chuck. Figure 40 shows variation in resistance at 650 °C with Figure 41 showing the mean deviation of the same data. This measurement was a standard contact resistance measurement where the probes were positioned at opposite corners of a metal bond pad.

The electrical probes can easily scratch the sample surface, which can short out traces, destroy bond pads, etc. Operators must exercise extreme care when connecting or disconnecting the electrical probes to minimize damage to the sample under test. The damage to samples is especially problematic for repeated tests as damage to bond pads or IDE structure may prevent further tests or change results in future tests. An example of damage to a sample caused by scratching is shown in Figure 42.

The system influences the test by introducing noise into the measured sensor response. Noise could possibly be introduced from thermal movement of the probe needles. It is speculated that thermal movement occurs from a thermal gradient that exists from the elevated temperature of the

heater to which the probe needles are in thermal contact and the micromanipulator mounting posts that are thermally connected to the base plate which is cooled by a water circulation system.

Figure 40. Contact resistance at 650 °C. Plot shows contact resistance measurements at 650 °C.

Figure 41. Mean deviation of contact resistance at 650 °C. This plot shows the mean deviation of the test data from Figure 40.

Figure 42. IDE structure coated with GaO_x with bond pads at lower corners showing damage from probe needle contact.

The cooling system is a recirculating type system which consists of: a 12 VDC pump with fan, radiator, reservoir, and heat exchanger. De-ionized (DI) water is pumped from the reservoir to the heat exchanger, then to the radiator before returning to the reservoir. The heat exchanger is an aluminum plate with a single horseshoe shaped path for cooling water. This plate is attached to the base of the test chamber. When the cooling system is engaged, noise in the $100 \text{ K}\Omega$ range increases dramatically. Figure 43 shows the same sample tested at identical conditions for 2 separate tests. One test used the cooling system, the other one did not. These results suggest that the cooling system introduces noise to the data acquisition system.

Figure 43. Plot shows noise introduced by cooling system using the same sample and test conditions for both tests. Blue line is data collected with cooling system on, where noise can be clearly observed. Red line is with cooling system off and less noise is visible in the sensor response.

Analysis of true temperature versus set-point for the heated chuck was used to determine the temperature error. The surface temperature of the heated chuck decreased at higher temperatures as compared to the thermocouple temperature. This error is not present at temperatures below 200 °C but increases steadily as the temperature rises to 650 °C, where it reaches an error of 25 °C. A graphical representation of the error between the surface temperature and the thermocouple temperature is shown in Figure 44.

Figure 44. Heated chuck temperature error. At temperatures above 200 °C, the actual surface temperature of the heated chuck was lower than the internal temperature. Below 200 °C the surface temperature matched the internal temperature. The difference at 650 °C is 25 °C, i.e., when the surface temperature is 650 °C the internal temperature is 675 °C.

CHAPTER 6

CONCLUSIONS

The Test Station designed and developed allows for meter flow of an individual test gas or groups up to 4 gasses at a time to be delivered to the test chamber. The 4 gas limit was principally due to financial limitations with the price of additional MFCs. Volumetric flow rate was found to be most effective in the range of 750 to 2400 SCCM. This range keeps *gas response time* reasonably low and does not consume too much gas which generally is a special order custom gas mix.

The Test Station allows for sample sensors to be exposed to test gasses in concentrations of less than one part per million (ppm) up to 100% source concentration. The concentration range is limited by the ability of gas manufactures to provide the original mix and purity of gas as all gas used in the Test Station was purchased from commercial vendors in cylindrical tanks.

The Test Station controls the heated chuck and thus the sensor temperature from room temperature to a maximum of 700 °C. The temperature of the Test Station is limited by the electric cartridge heaters contained in the heated chuck. These devices have a maximum temperature of 700 °C and for longer life should not be driven past 650 °C.

The Test Station connects external electrical measurement equipment to a sensor under test using probe needles, adjustable by micromanipulators. The probe needles fail after 20 to 30 uses due to ceramic adhesive mechanical failure. Additionally the hand made micromanipulators are not as accurate as machined versions would have been and are responsible for damage to sensors under test. Even for a skilled operator the damage can reduce the total number of separate tests to a sensor

to less than 5. The Test Station met the design criteria of humidifying the gas flow but at the cost of reduced *gas response time*. The H₂O bubbler is not an efficient path and due to increased piping lengths the *gas response time* more than doubles.

The Test Station is able to acquire and store resistance measurements from multiple sensors under test simultaneously. However, the Keithley DMM with slot additions did not provide for fast data acquisition rates when reading multiple channels. The DMM would respond to rapid communication signals for a single channel but required 550 ms per channel for multi channel reads. Electrical loading of the interdigitated electrodes should be investigated. Most sensors will experience distortion of the output when subject to a voltage potential [46].

The objective of this work was to construct a Test Station for the development of new microscale gas sensing devices suitable for application in exhaust gas streams of diesel engines and gas turbine engines used in power plants. The fabricated High Temperature Gas Sensor Testing Station met the requirements of the Project. Subsequent tests have shown that the Test Station operates within the design criteria. For thin film gas sensors, the Test Station environment mimics the conditions in the exhaust stream of a diesel engine. Furthermore, the Test Station was designed and fabricated for under \$20,000, well within budget.

The Test Station benefits scientists by enabling them to provide a test of the efficiency of prototype sensor devices. Providing reliable sensors to industry will enable scientists and engine manufacturers to better control emissions and thereby contribute to a cleaner environment and more efficient engines. Mankind will benefit from such studies as they will directly control the pollutants which are seriously affecting the planet.

REFERENCES

- [1] U. Alkemade, "Engines and Exhaust After Treatment Systems for Future Automotive Applications," *Solid State Ionics*, vol. 177, pp. 2291-2296, May 2006.
- [2] Cummins, "Cummins Demos Tech Roadmap for High-Efficiency, Clean Diesel Engine," Press release May, 2005.
- [3] U.S. EPA. (1970). Clean Air Act of 1970. U.S.C. Title 42, Ch. 85-I, Part A. Sec. 7401. Government Printing Office, U.S. Environmental Protection Agency, Washington, D.C.
- [4] P. Reichel, "Development of a Chemical Gas Sensor System," Ph.D. dissertation, Dept., Chem und Pharmazie, Eberhard Karls Universität Tübingen, Tübingen, Germany, 2005.
- [5] S.M. Sze, *Semiconductor Devices - Physics and Technology*, 2nd ed., Hoboken, NJ: Wiley, 1985.
- [6] D. Diamond, *Principles of Chemical and Biological Sensors*, vol. 150, New York: Wiley, 1998.
- [7] I. Hotovy, "Sensing Characteristics of NiO Thin Films as NO₂ Gas Sensor," *Thin Solid Films*, vol. 418, pp. 9-15, 2002.
- [8] H. Steffes, "Enhancement of NO₂ Sensing Properties of In₂O₃-based Thin Films Using an Au or Ti Surface Modification," *Sensors and Actuators B*, vol. 78, pp. 109-112, 2001.
- [9] N. Barsan, "Conduction Model of Metal Oxide Gas Sensors," *J. Electroceramics*, vol. 7, pp.143-167, Nov. 2001.
- [10] A. Tomchenko, "Semiconducting Metal Oxide Sensor Array for the Selective Detection of Combustion Gases," *Sensors and Actuators B*, vol. 93, pp. 126-134, 2003.
- [11] A. Mousa-Bahia, "A Gas Injector for an Automatic Environmental Test Chamber for the Characterization of Gas Sensors," *Sensors and Actuators B*, vol. 12, pp. 141-145, 1993.
- [12] EPA National Clean Diesel Campaign <http://www.epa.gov/cleandiesel/>
- [13] R. Bosch, *Diesel Engine Management - Systems and Components* 4th ed. West Sussex, England: R. Bosch GmbH, 2005, pp.463-464.
- [14] E. Sher, *Handbook of Air Pollution from Internal Combustion Engines - Pollution Formation and Control*, San Diego: Academic Press, 1998, ch. 6, pp. 122.

- [15] Z. Tang, "An Automated Precision Gas Sensor Characterization System," *IEEE International Conference on Microelectronics and VLSI*, pp.187 - 190, Nov. 1995.
- [16] M. S. Nieuwenhuizen, "An Automated SAW Gas Sensor Testing System," *Sensors and Actuators A*", vol. 44, pp. 219-229, 1994.
- [17] A. Vasile, "A Dedicated Data Acquisition and Monitor System for Measuring the Response Times of Gas Sensors," *Proceedings 1998 International Semiconductor Conference*, vol. 2, pp. 627-630, Oct. 1998.
- [18] J. Smulko, "The Measurement Setup for Gas Detection by Resistance Fluctuations of Gas Sensors," *Proceedings of the 2006 IEEE Instrumentation and Measurement Technology Conference*, vol. 24, pp. 2028-2031, Apr. 2006.
- [19] O. Figueroa, "Development of a Test System for Exhaust Gas Sensors in Streams with Large Temperature Fluctuations," M.S. thesis, Dept., Mat. Sci and Eng., Ohio State Univ., Columbus, OH, 2003.
- [20] F. Bender, "Characterization of a WO₃ Thin Film Chlorine Sensor," *Sensors and Actuators B*, vol. 77, pp. 281-286, 2001.
- [21] C. Delpha, "Humidity Dependence of a TGS Gas Sensor Array in an Air-conditioned Atmosphere," *Sensors and Actuators B*, vol. 59, pp. 255-259, 1999.
- [22] V. Dermene, "Integrated Semiconductor Gas Sensors Evaluation with an Automatic Test System," *Sensors and Actuators B1*, pp. 87-92, 1190.
- [23] R. Frank, (2008, Mar. 17). Hybrids vs. Clean Diesels. *Design News Mag.* pp. S1-S16.
- [24] O. Figueroa. "Temperature-controlled CO, CO₂, and NO_x Sensing in a Diesel Engine Exhaust Stream," *Sensors and Actuators B*, vol. 107, pp. 839-848, 2005.
- [25] M.B. Nix. (2007, July). Sniffing out Problems for Humans in Space. *IEEE Potentials Mag.* pp. 18-24.
- [26] S. Capone, "Solid State Gas Sensors: State of the Art and Future Activities," *J. of Optoelectronics and Advanced Materials*, vol. 5, pp. 1335-1348, Aug. 2003.
- [27] P. Moseley, "Solid State Gas Sensors - Review Article," *Meas. Sci. Technol.*, vol. 8, pp. 223-237, Sept. 1996.
- [28] J. Riegel, "Exhaust Gas Sensors for Automotive Emission Control - Review Article," *Solid State Ionics*, vol. 152-153, pp. 783-800, Mar. 2002.
- [29] M. Li, "An Investigation of Response Times of TiO₂ Thin Film Oxygen Sensors," *Sensors and Actuators B*, vol. 32, pp. 83-85, Feb. 1996.

- [30] A. Mandelis and C. Christofides, "Gas-Sensitive Solid State Semiconductor Sensors," in *Physics, Chemistry and Technology of Solid State Gas Sensor Devices*. New York, NY: Wiley, 1993, pp. 19-131.
- [31] I. Belov, "Thermal and Flow Analysis of SiC-based Gas Sensors for Automotive Applications," *Proceedings of the Thermal and Mechanical Stimulation and Experiments in Micro-electronics and Micro-Systems Conference*, vol 2, pp. 478-482, 2004.
- [32] L. Xiaojian, "Thermal-Power Consumption and Heat Transfer Coefficients in Micro-thin-film Gas Sensors," *Proceedings of the 2006 IEEE International Conference on Information Acquisition*, pp. 1311-1315, Aug. 2006.
- [33] F. Solzbacher, "A Comprehensive Analytical and Numerical Analysis of Transient and Static Hotplate Characteristics," *Proceedings of the 2003 International Conference on Solid State Sensors, Actuator, and Microsystems*, pp. 1856-1859, June 2003.
- [34] Z. Tang, "An Integrated Gas Sensor Based on Tin Oxide Thin-Film and Improved Micro-Hotplate," *Sensors and Actuators B* vol. 46, pp. 174 - 179, 1998 .
- [35] K. Ho, "Chemiresistor-type NO Gas Sensor based on Nickel Phthalocyanine Thin Films," *Sensors and Actuators B*, vol. 77, pp. 253-259, 2001.
- [36] Solidworks 3D CAD tool. 300 Baker Ave, Concord, MA, 01742.
- [37] A.J. Sedriks, *Corrosion of Stainless Steels*, 2nd ed. New York: Wiley, 1996.
- [38] P. Marshall, *Austenitic Stainless Steels - Microstructure and Mechanical Properties*, Essex, UK: Elsevier, 1984.
- [39] <http://www.hightempmetals.com/technicaldata.php>
- [40] Control System Design - Karl Johan Astrom, 2nd ed. 2002.
- [41] LabVIEW ver.7," National Instruments, Austin, TX, 2006.
- [42] "Celerity 8100 Series Specifications" Celerity Applications Engineering, Yorba Linda, CA., 2005.
- [43] Umwelt Sensor Technik NO sensor model 5000, Umwelt Sensor Technik, Dieselstraße 2 D-98716 Geschwenda, Germany.
- [44] Figaro NO Sensor model 2201, Figaro Inc. 3703 W. Lake Ave. Glenview, IL, 60025.
- [45] Watlow cartridge heater p/n J1J47-12K14J, Watlow Electric Manufacturing Company 12001 Lackland Road, St. Louis, MO, 63146.

- [46] J. Fraden, *Handbook of Modern Sensors - Physics, Designs, and Applications*, 2nd ed. New York: Springer-Verlag, 1996, pp. 494.