

# UC Berkeley

## UC Berkeley Electronic Theses and Dissertations

### Title

Environmental gas sensing with high surface area nanomaterials on a low-power microfabricated heater platform

### Permalink

<https://escholarship.org/uc/item/51w7t56x>

### Author

Harley-Trochimczyk, Anna Claire

### Publication Date

2016

Peer reviewed|Thesis/dissertation

Environmental gas sensing with high surface area nanomaterials on a low-power microfabricated heater platform

By

Anna Claire Harley-Trochimczyk

A dissertation submitted in partial satisfaction of the  
requirements for the degree of

Doctor of Philosophy

in

Chemical Engineering

in the

Graduate Division

of the University of California, Berkeley

Committee in charge:

Professor Roya Maboudian, Chair

Professor David B. Graves

Professor Liwei Lin

Summer 2016





## Abstract

Environmental gas sensing with high surface area nanomaterials on a low-power microfabricated heater platform

by

Anna Claire Harley-Trochimczyk

Doctor of Philosophy in Chemical Engineering

University of California, Berkeley

Professor Roya Maboudian, Chair

Gas sensors can provide information about the presence of dangerous gases in industrial and residential sites, allowing for improved environmental protection and human health and safety. In order to enable ubiquitous wireless monitoring of combustible and toxic gases, sensor elements with low power consumption are required. Two common types of gas sensors, namely calorimetric and conductometric sensors, rely on heated sensor elements to activate the appropriate reactions with the gas of interest, resulting in high power requirements to maintain the necessary operating temperatures. Miniaturized gas sensors made with microfabricated heater platforms and nanoscale sensing materials can lead to low power sensor elements with high performance. The minimization of the power consumption cannot be at the expense of the sensor's ability to detect dangerous combustible and toxic gases. The sensing performance is impacted by the properties of both the microheater and the sensing material, as well as the integration of the two elements, creating significant opportunity for research and development to improve the performance parameters, such as sensitivity, detectable concentration range, selectivity, response and recovery time, stability, size, manufacturability, and cost, as well as power consumption.

The development approach described in the following thesis relies on an optimized microheater platform as well as novel sensing materials. The design, fabrication, and characterization of a low-power microheater platform is described, with polycrystalline silicon as the heater material for moderate temperature and polycrystalline silicon carbide for improved reliability at high temperature operation. A small, isolated heated area decreases the required power consumption and a closed membrane facilitates easier deposition of sensing materials. Sensing materials for combustible and toxic gas detection have been developed based on ultra high surface area aerogels. For combustible gas sensing, graphene or boron nitride aerogel acts as a scaffold for catalytic platinum or palladium nanoparticles. Bare graphene aerogel and graphene aerogel coated with single to few-layer molybdenum disulfide sheets are used for toxic gas detection.

The microheater platform with fast response and recovery times provides opportunities for localized, in-situ synthesis of high surface area sensing materials. The use of the microheater platform for localized growth of a nanocrystalline tin oxide sensing film is described. The fast thermal response of the microheater leads to rapid heating of the precursor, creating a highly porous film that is proven beneficial for toxic gas sensing.

## Table of Contents

|                                                                                                          |           |
|----------------------------------------------------------------------------------------------------------|-----------|
| <b>CHAPTER 1. INTRODUCTION TO GAS SENSING.....</b>                                                       | <b>1</b>  |
| 1. BACKGROUND .....                                                                                      | 1         |
| 2. CALORIMETRIC SENSORS .....                                                                            | 1         |
| 3. CONDUCTOMETRIC SENSORS .....                                                                          | 3         |
| 4. SENSING PARAMETERS .....                                                                              | 5         |
| 5. OUTLINE OF THIS WORK .....                                                                            | 7         |
| <b>CHAPTER 2. POLYSILICON MICROHEATER FABRICATION AND CHARACTERIZATION ...</b>                           | <b>8</b>  |
| 1. BACKGROUND .....                                                                                      | 8         |
| 2. DESIGN CONSIDERATIONS .....                                                                           | 9         |
| 3. POLYSILICON MICROHEATER FABRICATION.....                                                              | 10        |
| 4. CHARACTERIZATION OF THE POLYSILICON MICROHEATER .....                                                 | 15        |
| 4.a. <i>Electrical characterization</i> .....                                                            | 15        |
| 4.b. <i>Temperature calibration</i> .....                                                                | 17        |
| 5. CONCLUSION .....                                                                                      | 21        |
| <b>CHAPTER 3. PLATINUM NANOPARTICLE-LOADED GRAPHENE AEROGEL FOR<br/>HYDROGEN SENSING.....</b>            | <b>22</b> |
| 1. MOTIVATION .....                                                                                      | 22        |
| 2. MATERIAL SYNTHESIS AND CHARACTERIZATION.....                                                          | 23        |
| 2.a. <i>Graphene aerogel</i> .....                                                                       | 23        |
| 2.b. <i>Platinum nanoparticle-loaded graphene aerogel</i> .....                                          | 23        |
| 3. DEVICE FABRICATION AND TEST METHODS .....                                                             | 24        |
| 3.a. <i>Integration of sensing material on microheater</i> .....                                         | 25        |
| 3.b. <i>Sensor measurements and gas delivery</i> .....                                                   | 25        |
| 4. SENSING RESULTS .....                                                                                 | 27        |
| 5. CONCLUSION .....                                                                                      | 33        |
| <b>CHAPTER 4. NANOPARTICLE-LOADED GRAPHENE AEROGEL FOR HYDROCARBON<br/>SENSING.....</b>                  | <b>34</b> |
| 1. MOTIVATION .....                                                                                      | 34        |
| 2. MATERIAL SYNTHESIS AND CHARACTERIZATION.....                                                          | 35        |
| 2.a. <i>Graphene aerogel</i> .....                                                                       | 35        |
| 2.b. <i>Platinum and palladium-nanoparticle loading</i> .....                                            | 36        |
| 3. SENSOR FABRICATION AND TESTING.....                                                                   | 37        |
| 4. SENSING RESULTS .....                                                                                 | 38        |
| 4.a. <i>Sensitivity and response time</i> .....                                                          | 38        |
| 4.b <i>Response stability</i> .....                                                                      | 40        |
| 5. CONCLUSIONS .....                                                                                     | 41        |
| <b>CHAPTER 5. PLATINUM NANOPARTICLE-LOADED BORON NITRIDE AEROGEL FOR<br/>CATALYTIC GAS SENSING .....</b> | <b>42</b> |
| 1. MOTIVATION .....                                                                                      | 42        |
| 2. MATERIAL SYNTHESIS AND CHARACTERIZATION.....                                                          | 43        |
| 3. SENSOR FABRICATION AND TESTING METHODS .....                                                          | 48        |
| 4. PROPANE SENSING PERFORMANCE.....                                                                      | 50        |
| 5. CONCLUSION .....                                                                                      | 54        |

|                                                                                                                       |            |
|-----------------------------------------------------------------------------------------------------------------------|------------|
| <b>CHAPTER 6. ROBUST CATALYTIC GAS SENSING USING HIGHLY STABLE SILICON CARBIDE MICROHEATERS .....</b>                 | <b>55</b>  |
| 1. MOTIVATION .....                                                                                                   | 55         |
| 2. MICROHEATER FABRICATION AND TESTING .....                                                                          | 56         |
| 2.a. <i>Silicon carbide microheater fabrication</i> .....                                                             | 56         |
| 2.b. <i>Microheater testing</i> .....                                                                                 | 57         |
| 3. SENSOR FABRICATION AND TESTING.....                                                                                | 58         |
| 4. RESULTS AND DISCUSSION .....                                                                                       | 59         |
| 4.a <i>Microheater characterization</i> .....                                                                         | 59         |
| 4.b. <i>Catalytic gas sensing performance</i> .....                                                                   | 62         |
| 5. CONCLUSIONS .....                                                                                                  | 66         |
| <b>CHAPTER 7. HIGH SURFACE AREA GRAPHENE AND GRAPHENE HYBRID AEROGELS FOR ULTRASENSITIVE GAS DETECTION .....</b>      | <b>67</b>  |
| 1. MOTIVATION .....                                                                                                   | 67         |
| 2. MATERIAL SYNTHESIS AND CHARACTERIZATION.....                                                                       | 68         |
| 2.a. <i>Synthesis of graphene aerogel, MoS<sub>2</sub> aerogel, and MoS<sub>2</sub>/graphene hybrid aerogel</i> ..... | 68         |
| 2.b. <i>Aerogel characterization</i> .....                                                                            | 70         |
| 3. SENSOR FABRICATION AND TESTING.....                                                                                | 72         |
| 4. GAS SENSING PERFORMANCE .....                                                                                      | 73         |
| 4.a. <i>Graphene aerogel</i> .....                                                                                    | 73         |
| 4.b <i>MoS<sub>2</sub>/graphene hybrid aerogel</i> .....                                                              | 77         |
| 5. CONCLUSION .....                                                                                                   | 81         |
| <b>CHAPTER 8. LOCALIZED GROWTH OF POROUS METAL OXIDE SENSING FILM ON MICROHEATER PLATFORM.....</b>                    | <b>84</b>  |
| 1. MOTIVATION .....                                                                                                   | 84         |
| 2. MATERIAL SYNTHESIS AND CHARACTERIZATION.....                                                                       | 85         |
| 3. LOW-TEMPERATURE CO DETECTION .....                                                                                 | 89         |
| 4. CONCLUSION .....                                                                                                   | 91         |
| <b>CHAPTER 9. CONCLUSIONS AND FUTURE OUTLOOK .....</b>                                                                | <b>92</b>  |
| <b>APPENDIX 1. METHANE SENSING .....</b>                                                                              | <b>94</b>  |
| 1. MOTIVATION .....                                                                                                   | 94         |
| 2. EXPERIMENTAL RESULTS.....                                                                                          | 95         |
| 3. THEORETICAL ANALYSIS.....                                                                                          | 97         |
| 4. CONCLUSIONS .....                                                                                                  | 99         |
| <b>BIBLIOGRAPHY .....</b>                                                                                             | <b>100</b> |

## Acknowledgements

I would like to express my appreciation to the many people who helped in my journey through graduate school and in the preparation of this dissertation. Thank you to my advisor, Prof. Roya Maboudian, for her continual guidance and steadfast support throughout my time at UC Berkeley. Additional thanks go to my committee members, Prof. David Graves and Prof. Liwei Lin, for their support and interesting conversations. I would also like to thank all of my research collaborators: Dr. William Mickelson, Hu Long, Thang Pham, Dr. Carlo Carraro, Dr. Marcus Worsley, Prof. Alex Zettl, Ernest Chen, Jeffrey Dong, Tianyi He, Ameya Rao, Dr. Qin Zhou and Dr. Jiyoung Chang. I believe that our exchange of ideas and interdisciplinary perspectives have resulted in more interesting research. Many other labmembers were immensely helpful and supportive in training me, troubleshooting with me, providing feedback on my presentations and papers, and making the lab an enjoyable place to work. These include Lunet Luna, Leslie Chan, Peter Lobaccaro, Albert Gutes, Ben Hsia, John Alper, Yongkwan Kim, Allen Sussman, Wenjun Yan, Yuan Gao, Hai Liu, Arthur Montazeri, Gina Zaghi, Raphael Brechbuhler, Sinem Ortabay, Steven Delacruz, and Ye Tian.

I would like to acknowledge the efforts of the staff in the department, the College of Chemistry, and the entire university, with special appreciation for Carlet Altamirano, who had an answer for every question and enthusiastic assistance in finding the answers when she did not. Kristin Stangl and Joel Adlen were also especially helpful in the logistics of acquiring research materials.

These research efforts have been supported by the National Science Foundation through the Graduate Research Fellowship Program (DGE 1106400), the Innovation Corps program (Award No. 1357682), and the Accelerating Innovation Research: Technology Transfer program (IIP 1444950). Additional support has come from the Center of Integrated Nanomechanical Systems (COINS) and the Berkeley Sensor and Actuator Center (BSAC).

Personal gratitude goes to my fellow graduate students in the Department of Chemical Engineering and the rest of the university who were there for me with advice and commiseration in the hard times that inevitably occur during the pursuit of a PhD. Our department is lucky to have such a supportive and cohesive group of students, something I cherish and hope that future students will cherish as well. I would also like to thank my family members who have always been my biggest cheerleaders. My mom and dad are the source of my work ethic, my ambition, and my intellectual curiosity. My brothers have always been great reminders of the value of balance and of laughter. A final acknowledgement goes to Chris, who deserves at least 10% of the credit for this dissertation. All of my best ideas come from our discussions.

# Chapter 1. Introduction to Gas Sensing

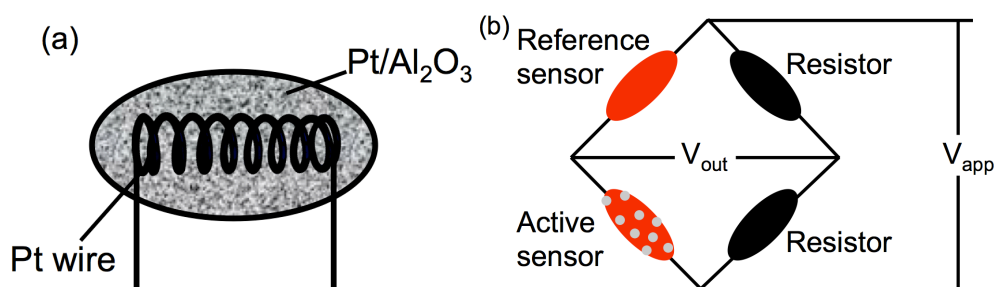
## 1. Background

Starting from the days of the canary in the coal mine, technologies have been developed to assist with the detection of gases, whether they be toxic, combustible, or simply contain an unpleasant odor. At the core of gas sensor development is the exploitation of some chemical or physical property of the gas to detect its presence. There are several broad classes of techniques, each with its own advantages and limitations, including electrochemical sensors, conductometric sensors, calorimetric sensors, optical sensors, acoustic sensors, and more. To ease the interface of the chemical or physical property change to electronic machinery, most sensing techniques depend on the transduction of the chemical interaction to an electronic signal. The two techniques in particular that are the focus of this work are calorimetric and conductometric sensing. In calorimetric sensing, the presence of the gas of interest creates a temperature change in the sensor that is detected as a resistance change, as determined by the temperature coefficient of resistance of the sensing material. Conductometric sensing is a more direct measurement, where the target gas adsorption on the sensing material results in a resistivity change of the sensing material. Both techniques rely on heating a material that is sensitive to a particular gas interaction, so the power consumption tends to be high. Relevant parameters for gas sensor development include size, power consumption, sensitivity, selectivity, limit of detection, response and recovery time, manufacturability, cost, and stability. Rarely can a particular technology have great features in each of these categories, rather the particular features of importance for each application must be decided. Because of the wide parameter space and the complexity of the applications for gas sensors, this is an active area of research and development.

## 2. Calorimetric sensors

The basis of calorimetric sensors is the detection of a temperature change in the sensor element, which is made of a material that has a high temperature coefficient of resistance, such that the temperature change creates a change in resistance that can be easily measured with an electrical circuit [1], [2]. The most common sensor of this kind is for combustible gas measurement. The basic operation of the calorimetric combustible gas sensor, also called a pellistor or catalytic bead sensor, is shown in Figure 1. A catalytic material is heated to high temperature (a few hundred °C). The target gas adsorbs on the catalyst surface and is oxidized in an exothermic reaction. The subsequently produced heat increases the temperature of the sensing element, which changes the resistance [3], [4]. The earliest version of this type of sensor was simply a platinum wire [5]. By passing a current through the wire, it heats up through Joule heating. At high temperature, hydrocarbons and other combustible gases react on the surface of the platinum wire and increase the temperature, and therefore, the resistance. However, the stability of the sensor was poor and the sensitivity low. Platinum and other noble metals like palladium are the catalyst of choice for hydrocarbon oxidation [6]–[8], and progress in catalyst development for other applications, such as catalytic converters and petroleum plants, made its way to gas sensors as well. The next iteration of the sensor saw a platinum wire coated in a porous alumina coating that has platinum nanoparticle dispersed on it. The platinum nanoparticles had higher activity for hydrocarbon oxidation than the platinum wire, so lower temperatures could be used and the platinum wire transducer could be more stable [5].

The pellistor sensor element is most often employed in a Wheatstone bridge configuration, with a reference sensor element that is identical in construction except the porous alumina does not have platinum nanoparticles dispersed in it. In this way, changes in ambient conditions such as humidity or ambient temperature, or a change in thermal conductivity of the surrounding gas can be offset [1].



**Figure 1.** (a) Pellistor schematic showing platinum wire coil coated with platinum nanoparticle-loaded alumina. (b) Wheatstone bridge sensing configuration with two heated elements, the active sensor and the reference sensor, which does not have platinum nanoparticles loaded in the alumina.

One of the main limitations of the pellistor is the high power consumption. The use of a platinum wire limits the miniaturization potential, leading to sensor elements with a length of a few mm. The power consumption limits the ability of the sensor to be used in a wireless capacity when battery-powered. In the interest of improving the monitoring the environmental conditions in industrial and residential sites, researchers have pursued the development of low power versions of this technology. In order to lower the power requirements of heated sensors for combustible or toxic gas sensing, either the size of the sensor must be decreased or the temperature required for detection must be decreased. Development of catalysts effective for hydrocarbon combustion at temperatures lower than 500 °C have not been successful [8], so researchers have focused on the miniaturization of the heater element, leveraging microfabrication technologies to define small features [9]–[14].

In a typical microfabricated catalytic gas sensor, there is a heater trace embedded in a silicon nitride membrane with a catalytic material deposited on top [10], [15]–[19]. Often the heater element is also the temperature sensor, but in some cases, the functions are split. Typical heater materials are platinum and polysilicon because they have appreciable temperature coefficients of resistance and can operate to moderately high temperatures [20]–[23]. Silicon nitride can be deposited in thin films with low stress, which allows for stable membranes that thermally isolate the heater from the substrate. Microheater power consumption depends on the size of the heated area and the thermal isolation, which includes the geometry of the device as well as material properties such as thermal conductivity. Despite the advancements in the microheater development, platinum nanoparticle loaded alumina remains the catalyst material of choice. The adhesion of the catalyst material onto the platform and the thermal conductivity of the support affect the required power consumption to get the catalyst to the appropriate temperature [24]. The sensitivity of the measurement relies on the temperature coefficient of resistance of the

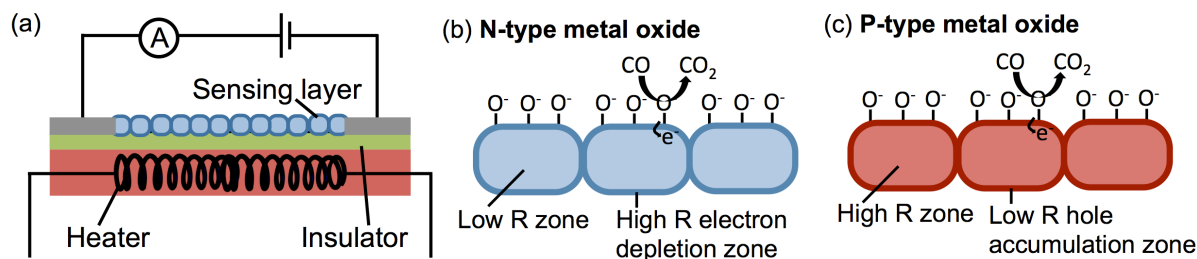
temperature sensor element, the noise in the temperature sensor element, the efficiency of the heat transfer from the catalyst to the temperature sensor, the amount of catalyst surface area, and the accessibility of the catalyst for the target gas of interest.

The number of factors impacting the measurement provides many possibilities for optimization. For example, the approach taken by Brauns, et al., seeks to eliminate the need for a support material by stabilizing the platinum nanoparticles with organic ligands in order to improve the heat transfer and therefore, the sensitivity [25]–[27]. The organic ligands are not thermally stable to high temperatures, which limits their use for hydrogen detection, which can be done at fairly low temperature (200 °C). Others developed a highly sensitive thermopile to detect temperature changes  $<1$  °C [28], [29]. Xu, et al., developed a suspended heater structure with a concave shape to contain the catalytic material to improve the heating efficiency [30]. Barsony, et al., investigated a number of different noble metals catalysts on various oxide supports and concluded that the adhesion of the support to the microheater remained a challenge [15].

### 3. Conductometric sensors

The basis for conductometric sensing is the measurement of a change in resistivity in a heated sensitive material when exposed to the gas of interest (Figure 2a). The sensing mechanism is quite complex and the details change with the particular sensing film and target gas. At the simplest level, the interaction (adsorption or reaction with other surface species) of the target gas with the surface of the conductive film results in a conductance change through the film [31]. The details rely on the exact nature of the conductive film, the target gas of interest, and the environment (e.g. sensing in air vs. inert gas or humidity). The earliest sensors of this type relied on tin oxide as the conductive film [32], [33]. For sensors based on an n-type tin oxide film, adsorbed oxygen species draw electrons from the tin oxide, creating a depletion zone at the surface of the tin oxide crystals (Figure 2b). As the target gas of interest arrives at the sensor, it displaces or reacts with the surface oxygen species, decreasing the depletion zone and lowering the resistance of the sensor [33]. A p-type metal oxide has a response of the opposite sign. Because the majority carriers in a p-type material are holes, the adsorbed oxygen species draw electrons from the oxide, generating a low resistance hole accumulation zone near the surface (Figure 2c). As the target gas arrives and displaces the adsorbed oxygen, it releases electrons, which increases the resistance of the sensor [34]. The response and recovery times for the conductometric sensor tend to be longer than the calorimetric sensor because the response does not stabilize until the adsorption and reaction of the various gases reaches equilibrium. Heating the sensing film can improve the response and recovery time by speeding up the gas desorption, which allows the equilibrium point to be reached more quickly. For tin oxide films, operating at elevated temperatures also changes which surface oxygen species are favored [35], [36]. The varied levels of reactivity of the different surface oxygen species with the target gas can also change the sensitivity [37]. Sensitivity is also affected by the metal oxide grain size, number of grain boundaries in the conductive path, film thickness, and doping level [33], [34]. Common strategies to engineer improved sensitivity or selectivity also include decoration with metallic nanoparticles or formation of p-n junctions through combinations of metal oxides [38].





**Figure 2.** (a) Conductometric sensor structure with conductive sensing layer and separate heater channel. (b) Adsorbed oxygen species on n-type metal oxide create a high resistance electron depletion zone. CO exposure results in a decrease in resistance. (c) Adsorbed oxygen species on p-type metal oxide create a low resistance hole accumulation zone. Upon exposure to a reducing gas like CO, electrons are donated to the material, increasing the resistance.

A recent explosion of research interest in two-dimensional materials like graphene and transition metal dichalcogenides includes their use as conductometric sensor materials [39]–[41]. Conductive two-dimensional single layer materials have the absolute highest surface area to volume ratio, which means that the material properties are highly affected by the state of the material surface. Schedin, et al, even demonstrated single molecule gas detection with single-layer exfoliated graphene [42]. In the case of these two-dimensional materials, the sensing mechanism is thought to be from the direct adsorption of the gas of interest. For example, nitrogen dioxide is a known electron acceptor because of the unpaired valence electron on the nitrogen [43]. When NO<sub>2</sub> adsorbs on a p-type material surface, it withdraws electrons, which increases the number of holes (the majority carrier in p-type materials) and lowers the resistance. Although pristine exfoliated graphene should be undoped, common processing steps leave it p-doped [44]. Single-layer two-dimensional materials have shown gas response at room temperature, but the response and recovery are often very slow [42], [45]–[50]. Energy input through heating or illuminating with UV light are required to improve desorption [51]–[54]. Sensitivity is impacted by the number and type of defects in the material, as these tend to interact more strongly with adsorbed gas molecules [55], [56], and the operating temperature. Sensitivity and selectivity can also be improved through functionalization or decoration [57].

Table 1 shows a comparison of the performance of calorimetric and conductometric sensors for the relevant target gases, required operating temperatures, and role of oxygen in the sensing mechanism. Both metal oxide and 2D materials for conductometric sensing are included since they have significant differences in mechanism.

**Table 1.** Comparison of calorimetric and conductometric sensors

|                        | Calorimetric       | Conductometric                                                               |              |
|------------------------|--------------------|------------------------------------------------------------------------------|--------------|
|                        |                    | Metal oxide                                                                  | 2D materials |
| Target Gases           | Hydrocarbons, VOCs | Toxic gases (CO, NO <sub>2</sub> , NH <sub>3</sub> , H <sub>2</sub> S), VOCs |              |
| Operating Temperatures | 300-500 °C         | 200-400 °C                                                                   | RT – 300 °C  |
| Oxygen Required?       | Yes                | Yes                                                                          | No           |

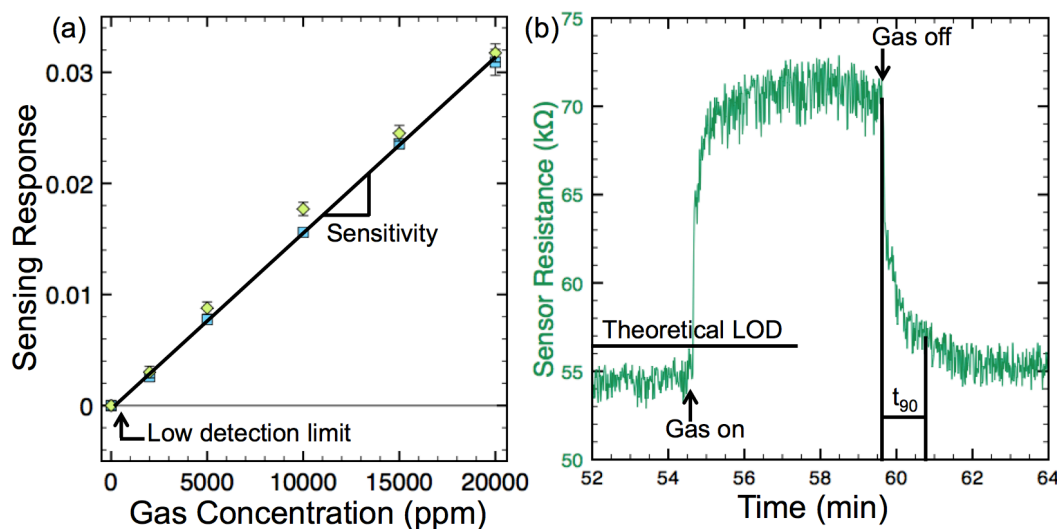
#### 4. Sensing parameters

In the following investigation, a number of the sensing parameters are quantified according to the definitions presented here. The power consumption is calculated from the applied potential to the heater and the heater resistance in clean air:

$$P = V^2/R \quad (1)$$

The sensor transforms the chemical change in the gas phase to an electrical change, so the raw sensor output is the resistance. To compensate for changes in the baseline resistance,  $R_0$ , and to make it easier to compare sensors with different baseline values, the resistance during gas exposure,  $R_{\text{gas}}$ , is usually normalized to the baseline. So the sensor response is calculated either as a ratio ( $R_{\text{gas}}/R_0$  or  $R_0/R_{\text{gas}}$ ) or as a percentage ( $(R_{\text{gas}}-R_0)/R_0 \times 100\%$ ) depending on whether a signal of 0 or 1 is preferable for the zero concentration point [58]. The conditions for  $R_0$  are reported, including humidity level and temperature, because these factors will affect the baseline value.

When the sensor response is plotted versus the gas concentration, the sensitivity or slope can be calculated. A sensor with high sensitivity can more easily distinguish between two close concentrations and tend to have lower limits of detection (LOD), which is the lowest detectable concentration (Figure 3a). The limit of detection can be determined theoretically using the average and standard deviation of the sensor baseline and a standard signal-to-noise ratio of 3 [59]. Figure 3b shows the resistance level that would be considered the theoretical limit of detection, which is 3 times the standard deviation of the baseline above the baseline level. The corresponding concentration is calculated with a linear interpolation from 0 ppm to the lowest gas concentration delivered. In some of the investigations presented here, the lowest deliverable gas concentration is higher than the limit of detection, and this level is specified as the experimental limit of detection. The source of the limitation is the accuracy of the mass flow controllers used for gas delivery. The response and recovery times are always reported as the time to reach 90% of the signal or recovery ( $t_{90}$ ). The time is calculated from the start of the gas exposure to the time when 90% of the signal is reached, as shown in Figure 3b. For sensors that have very fast response, frequent data collection is required to give precision to this calculation. To calculate proper response and recovery times, the sensor must reach a stable value. Otherwise the 90% response is determined by the time of gas exposure and represents the testing parameters selected rather than a true property of the sensor.



**Figure 3.** (a) Response versus concentration curve showing the sensitivity (slope of the linear fit) and limit of detection (LOD). (b) Sensor resistance over time during gas exposure showing the theoretical LOD level and  $t_{90}$  recovery time.

In order to determine selectivity, the sensor is exposed to various gases at the same operating temperature and the response to different gases is compared. Selectivity factors are unnecessary for this investigative work, but are regularly calculated for commercial sensors.

## 5. Outline of this work

Both calorimetric and conductometric sensing require heating for best performance (Table 1), but wireless sensor networks require sensors with low power consumption in order to be battery-powered for a reasonable length of time. In this work, a microheater element is developed with a small heated area to minimize power consumption using a doped semiconductor, silicon for moderate operating temperatures and silicon carbide for high operating temperatures. Using a semiconductor in place of platinum as the heater material allows for heat dissipation in a small trace with no fear of electromigration issues, as well as allowing tunable resistivity and temperature coefficient of resistance values. The fast thermal response of the developed microheater also allows for duty cycling, where the heater is turned on for a fraction of a second to collect information and then turned off to conserve power. The design, fabrication, and characterization of the polysilicon microheater platform is discussed in Chapter 2. The polysilicon carbide microheater, which offers improved stability at high temperature, is discussed in detail within Chapter 6.

In addition to the low power microheater platform, new sensing materials are needed to truly enable useful gas sensing performance. For combustible gas sensing, novel catalytic materials based on ultra high surface area graphene and boron nitride aerogels are investigated. The aerogels offer high loading of catalytic platinum or palladium nanoparticles with minimal support mass and high thermal conductivity compared to traditional materials like alumina, which allows for more efficient heat transfer. Chapter 3 focuses on the use of platinum nanoparticle-loaded graphene aerogel on the polysilicon microheater for hydrogen detection.

Chapter 4 extends the study to propane gas with platinum and palladium-loaded graphene aerogel with higher thermal stability, thanks to a high temperature anneal synthesis step. The two materials give different responses, demonstrating the ability to create a sensor array for more selective gas measurements. Chapter 5 presents the synthesis and use of platinum-nanoparticle loaded boron nitride aerogel for propane detection, showing improved response stability, due to the thermal stability of the boron nitride aerogel. All of these show fast response and recovery times and no loss in sensitivity during duty cycling, such that the measurement requires 1-2 mW with data still collected every 1-2 s, which is a power consumption two orders of magnitude lower than the best commercially available combustible gas sensor.

For conductometric gas sensing, new materials based on the highly conductive graphene aerogel can be integrated onto the polysilicon microheater and used to monitor toxic gases. Chapter 7 presents the sensing properties of bare graphene aerogel for gases like nitrogen dioxide, carbon monoxide, and hydrogen. Coating the graphene aerogel with single to few-layers  $\text{MoS}_2$  sheets improves the selectivity to nitrogen dioxide while maintaining high sensitivity, an ultra low detection limit, and fast response and recovery time when heated. The use of hybrid aerogels with the graphene aerogel lending high surface area, high electrical and thermal conductivity, and the two-dimensional material coating lending selectivity and sensitivity is a very interesting strategy for future sensing material development as well. In Chapter 8, the thermal properties of the microheater platform are used to locally synthesize a highly porous, nanocrystalline tin oxide film with high performance for carbon monoxide sensing. A liquid tin oxide precursor is dropped on the microheater platform and rapidly heated to evaporate the solvent and form the solid metal oxide nanoparticles. The rapid heating rate of the microheater helps maintain the porosity of the film and small size of the tin oxide particles, which leads to a highly sensitive sensor element with fast response and recovery time as well. Besides contributing to low power performance during sensing measurement, the microheater platform is useful in synthesizing sensing materials in a localized manner that can simplify manufacturing of these types of elements.

Finally, conclusions and future outlook for this research effort are presented in Chapter 9.

## Chapter 2. Polysilicon Microheater Fabrication and Characterization<sup>1</sup>

### 1. Background

In order to lower the power requirements of heated sensors for combustible gas sensing, either the size of the sensor must be decreased or the temperature required for detection must be decreased. Development of catalysts effective for hydrocarbon combustion at temperatures lower than 500 °C have not been successful [8]. The use of MEMS technology makes heater miniaturization possible. The first efforts to develop a microfabricated combustible gas sensor by Gall in 1991 led to design with a metal trace that acted as heater, temperature sensor, and catalyst evaporated onto a silicon nitride membrane [9]. The device relies on Joule heating by driving current through the metal trace. The membrane thermally isolates the heated area so that high temperatures could be achieved with low power. This basic initial design soon led to a splitting of the heating and temperature sensing functions from the catalysis for increased stability and the ability to optimize materials for the various functions independently. A typical early design of this type is a platinum heater embedded within two layers of silicon nitride with a catalyst suspended in a porous support deposited above [10], [15], [60]. Insulating the heater from the atmosphere leads to improved lifetime. Platinum is a common choice for the combined heater and temperature sensor because of its chemically inert nature and high temperature coefficient of resistance. However, platinum has poor adhesion to the most common membrane materials ( $\text{Si}_x\text{N}_y$ ,  $\text{SiO}_2$ , Si) [61], especially at the required operating temperatures. Other problems with platinum include resistance drift at high temperatures ( $>500$  °C) [62], and limited maximum current densities of  $10^5$ - $10^7$  A  $\text{cm}^{-2}$  imposed primarily by the phenomenon of electro-migration, which occurs when conducting electrons transfer momentum to atoms in the conductor, causing undesired material transport [63]. Due to these problems, Pt-based microheaters require long conductive paths, which limit the miniaturization of the heater element. Semiconductor materials like polysilicon have higher resistivity that is tunable with doping level, allowing for more efficient heat dissipation in a smaller area. Silicon also resists electro-migration and has a similar thermal coefficient of expansion to silicon nitride, decreasing membrane stress during operation.

Modern microheater technologies can be evaluated on the basis of heated area, power consumption, heater resistance stability, mechanical robustness, and temperature uniformity, among other factors. There is great diversity in design and choice of materials for microheaters intended for sensing applications in the literature. In this chapter, the particular design of our microheater platform will be motivated and the fabrication process and characterization will be described. The microheater platform is designed to be functional for both combustible gas sensing and conductometric sensing.

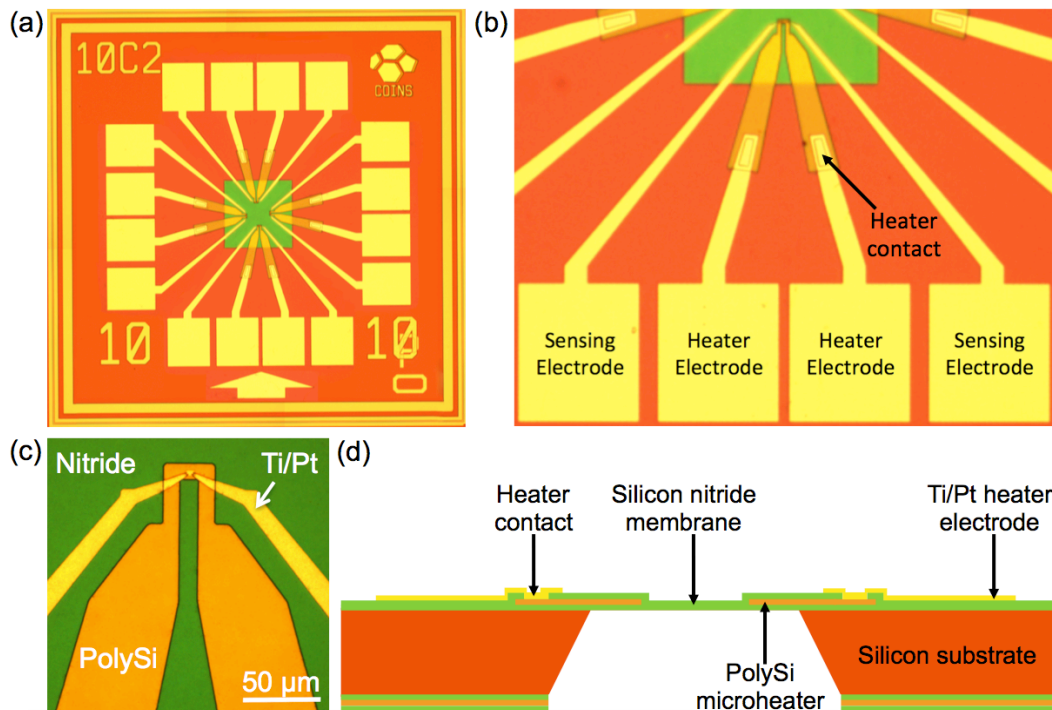
---

<sup>1</sup> Dr. Jiyoun Chang and Dr. Qin Zhou assisted with the design and fabrication process development for the polysilicon microheaters.

## 2. Design considerations

The current microheater design, as shown in Figure 1, relies on a thin polysilicon trace embedded in silicon nitride. Polysilicon is used as the heater material because of its tunable high conductivity, resistance to electro-migration, compatibility with MEMS processing, and good temperature coefficient of resistance. Silicon nitride is used as the membrane material because it can have low stress, which allows it to have a large area to thickness ratio without buckling. Platinum with a titanium adhesion layer is used as the heater contact and sensing electrode material. The titanium layer improves the electrical contact by forming a titanium silicide at the heater contact interface. Elsewhere, it improves the adhesion of the platinum to the silicon nitride. The platinum has a high resistance to oxidation, so a stable contact can be maintained. The heater contact and sensing electrodes are made from the same material because it decreases the process complexity by lowering the number of masks needed.

One major change is the use of a closed membrane or a continuous membrane that contacts the substrate at all edges, instead of a beam structure that only contacts the substrate at a few points. This design increases the power consumption because the membrane provides more area for heat loss to the substrate. But on the other hand, it allows for easier deposition of sensing material from a liquid suspension without the problem of solvent wicking into a cavity below the microheater. The closed membrane is fabricated through a back-side etch, during which the front-side of the wafer (including the heater contacts) is coated by an alkaline resistant coating.



**Figure 1.** Polysilicon microheater design. (a) Optical image of the entire microheater chip (3.5 x 3.5 mm) with four microheater elements. (b) An image of one microheater showing the sensing and heater electrodes. (c) One microheater element, where the U-shape is the heated area. (d) A cross-sectional schematic of the chip.

In order to have four microheaters suspended in the same membrane, the heater is not a straight beam, but rather a U shape with both heater contacts on the same side of the membrane. The polysilicon heater trace has a width of 10  $\mu\text{m}$  and a thickness of 100 nm, in a silicon nitride membrane with a thickness of approximately 200 nm and total area of 400 x 400  $\mu\text{m}^2$ . The membrane should be as thin as possible and as large as possible to improve the thermal isolation of the heater element. The sensing electrodes have a small gap of only 4  $\mu\text{m}$  in the middle of the microheater, such that the conductive path through the sensing material travels through only the heated material. For combustible gas sensing where the sensing electrodes are not used, they are masked with silicon dioxide. The total chip size is 3.5 x 3.5  $\text{mm}^2$ , which gives lots of space for the heater contacts to be set back from the membrane so that they do not heat substantially, leading to improved contact stability. The sensing electrodes are placed far away from the heater contacts to help minimize shorting. Four microheaters are placed on one chip in order to allow for a single chip array of sensing materials and have the added benefit of increasing redundancy in the case where only one sensing material is being evaluated.

### 3. Polysilicon microheater fabrication

Microheater fabrication is done in the Marvell Nanofabrication Laboratory at UC Berkeley. The following will have a high degree of process specification with the intention of simplifying efforts of future researchers in using a similar process. Figure 2 shows a schematic of the overall process flow, which uses 4 masks. All processing is done on 4-inch double-side polished p-type silicon wafers.

To start, the silicon wafers are cleaned with a piranha bath etch (10 minutes) and HF dip (4.9% or 10:1 dilution, 30 s) in *msink8* and *msink6* with appropriate rinse and drying steps. Optical inspection for any remaining particles is done before loading into the furnace. The wafers are loaded in *tystar17*, the low-pressure chemical vapor deposition furnace for silicon nitride deposition. Using dichlorosilane and ammonia precursor gases and the standard deposition recipe, a low stress silicon-rich film of silicon nitride is deposited. Film thickness is confirmed with *nanospec*, which measures the light reflected from the wafer as a function of incident wavelength to calculate a film thickness, given the index of refraction of the thin film material [64]. This measurement technique works well only for optically transparent films in the thickness range of 10 to 4000 nm [64]. For the silicon nitride growth, film thickness varies about 5 nm from the middle of the 4-inch wafer to the edge for an average film thickness of 120 nm. The average film thickness also varies by position in the furnace with thicker films on the wafers closer to the gas source. For a deposition time of 25 minutes with the standard recipe, the film thickness is approximately 120 nm, subject to the variations previously discussed. Good practice includes growing nitride on a dummy wafer that can be used to characterize the film stress and etching rate. For stress measurement, *flexus* measures wafer curvature before and after deposition and then calculates the film stress from the curvature change, given the film thickness [65], [66]. To take this measurement, the curvature of one wafer needs to be measured before it goes into the furnace and the same one measured afterward (once the backside film is etched off, so only the front-side film growth impacts the curvature). Each wafer should be marked with a scribe in an unimportant location for ease of tracking in these process measurements.

After the nitride deposition and characterization, a doped polysilicon film is deposited on the wafers (Figure 2a). If this step does not occur soon after the wafers are removed from the nitride furnace, then the wafers need to go through the *msink8/msink6* cleaning process again. Low-pressure chemical vapor deposition of polysilicon in *tystar16* is done with silane gas as the silicon source, phosphine gas as the phosphorous dopant source, and nitrogen as the carrier gas. Using the standard doped polysilicon recipe with a deposition time of 60 minutes yields a film with a thickness of approximately 100 nm. Again, for ease of process measurement, adding a clean dummy wafer helps with film thickness and stress measurement. Resistivity measurement can be done on process wafers with *4ptprb*, an automated four-point probe measurement tool [67], which reports the sheet resistance in  $\Omega$  per square. The resistivity can be found by multiplying by the film thickness.

The first mask is now used to define the microheaters in the doped polysilicon layer. The wafers are coated with hexamethyldisiloxane (HMDS) to improve photoresist adhesion using *primeoven*. Photoresist coating is done with an automated spin-coater tool called *svgcoat2*, designed for 4-inch wafers. Positive i-line resist (FujiFilm OiR 906-12) is used, which requires 365 nm UV light for exposure. For positive photoresist, wherever the light hits, the resist is removed when developed. The spin speed and time determine the photoresist thickness in the spin coating process, and for the standard recipe, a thickness of 1.2  $\mu\text{m}$  is expected. The spin-coat is followed by a bake at 90 °C for 60 s, also using *svgcoat2*. Alternately, manual HMDS coating, photoresist coating, and bake can be done using *msink3*, *headway1* or 2, and the hot plates next to *msink1*. The photoresist exposure is done using a contact alignment tool, *ksaligner*, which has feature resolution of 1  $\mu\text{m}$ . The total exposure dose for the i-line resist is 150  $\text{mJ}/\text{cm}^2$  with hard contact, so the wafer is in direct contact with the mask during exposure. Given that the UV lamp intensity varies over its lifetime, a new exposure time needs to be calculated for the session using the most recent intensity measurement posted in the tool notes by Nanolab staff. For a polished wafer, it should not be a consideration, but be aware that surface roughness impacts exposure and a rough surface may require some trial before an appropriate exposure time is obtained. A post exposure bake at 120 °C for 60 s needs to be done before development. Standard i-line photoresist developer is available in the Nanolab and requires a 60 s develop time at *msink1* or *svgdev2* with agitation and a de-ionized water rinse. Visual confirmation of the development marks and heater features should follow. Completing the develop step for one wafer before exposing other wafers is recommended because it allows for adjustments to be made with the exposure time. If there are any issues with the photoresist coating, exposure, or development steps, the photoresist needs to be stripped and the process repeated. Photoresist stripping can be done in the PRS-3000 baths at *msink3*, followed by de-ionized (DI) water rinse and spin-drying. If the wafer layers are compatible, another piranha dip and rinse/dry can be considered to remove any residual organic material.

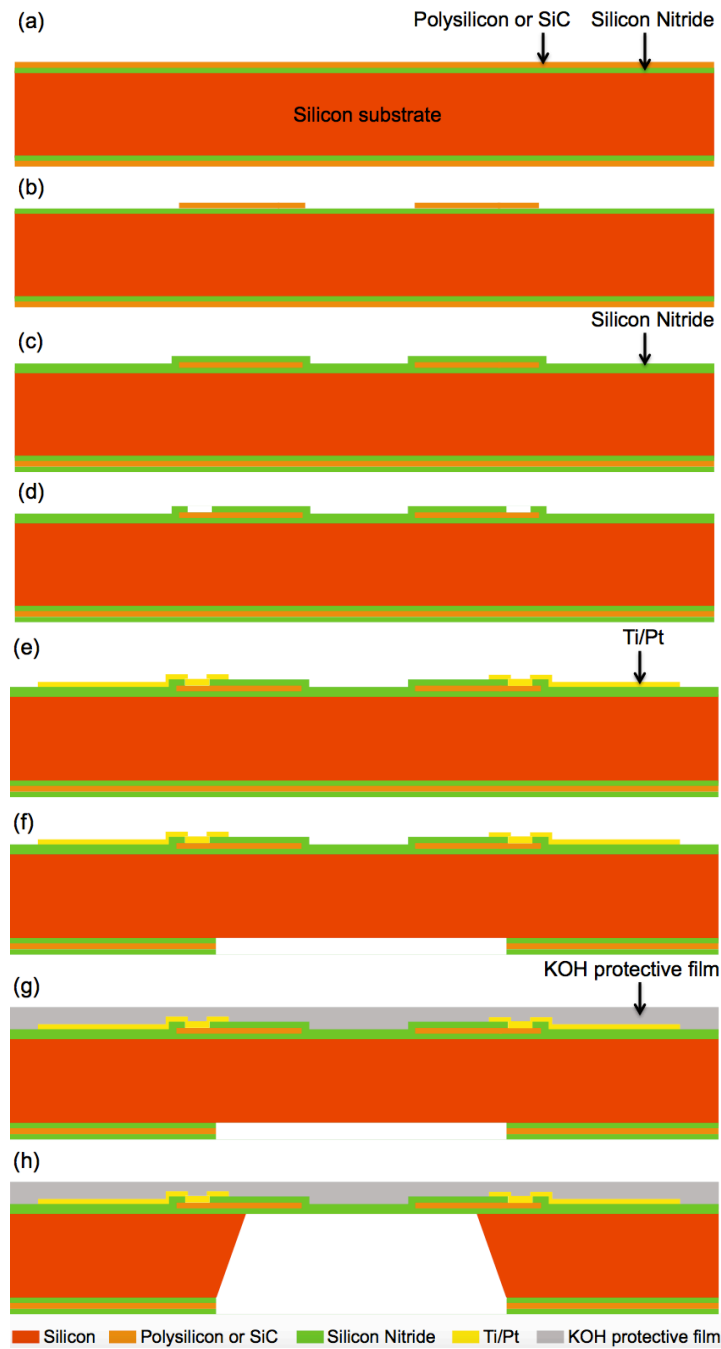
The developed photoresist acts as a mask for the polysilicon during the plasma etch (Figure 2b). Polysilicon etch is done in *ptherm* with a 90/10 mixture of  $\text{SF}_6$  and  $\text{O}_2$  gases with a total flow rate of 90 sccm and a plasma power of 100 W. Etch rates vary with tool history so it is best to first run an  $\text{O}_2$  plasma cleaning step and then run a dummy wafer to confirm the etch rate. For example, run for half of the expected etch time, and then check the thickness of the remaining



polysilicon. Silicon nitride has a high etch rate with  $\text{SF}_6/\text{O}_2$  [68], hence care must be taken not to over-etch the polysilicon too much or the silicon nitride membrane underneath may be completely removed as well. Etch effectiveness can be measured a few different ways. After removing the photoresist, a visual inspection should reveal the microheater features. Profilometry using *asiq* can give the step height of the microheater features [69], [70], which should be slightly larger than the polysilicon film thickness. Interference measurement with *nanospec* can be used to determine whether there is any remaining polysilicon in a feature-less area of the wafer and a 4-point probe measurement on the same area should give no measurement since the exposed silicon nitride is not conductive.

After stripping the photoresist and cleaning the wafers, a second deposition of low-stress silicon nitride is done with the same parameters as the first deposition (Figure 2c). The thickness of this film should also be monitored on a dummy wafer, which will also be used to determine etch rates in the next etch step. The second mask is used to define windows in the top silicon nitride layer so that the heater material can be contacted with metal (Figure 2d). The same photoresist processing is used as the first mask. Since only small features in the photoresist will be developed away, the HMDS coating is especially important to ensure photoresist adhesion. The second mask is aligned to the first mask with the alignment marks. Visual inspection should show the windows above the ends of the microheaters. Plasma etch of the silicon nitride layer is done with a mixture of helium,  $\text{CF}_4$ , and  $\text{CHF}_3$  gases (100 sccm, 75 sccm, and 25 sccm, respectively). At 100 W plasma power, the etch rate is about 0.7 nm/s, but this should be verified before running process wafers because  $\text{CF}_4$  is a known etchant for polysilicon as well [68]. After stripping the photoresist, the nitride etch can be confirmed as described previously.

The third mask is used to define the metal contacts (Figure 2e). A negative photoresist (Futurrex, NR9-1500PY) is spun onto the clean wafer with the manual spin coater (*headway2*). The spin coat is done at 3000 rpm for 40 s with a 1000 rpm  $\text{s}^{-1}$  ramp, followed by a bake at 150 °C for 60 s. For negative photoresist, wherever the light is blocked, the resist is removed when developed. The metallization process requires the photoresist remain wherever the metal is not wanted, such that after metal evaporation on the whole wafer, the photoresist is dissolved away, removing the undesired metal. Contact alignment and exposure is done with a total exposure dose of 190  $\text{mJ}/\text{cm}^2$  and is followed by a post-exposure bake of 120 °C for 60 s. In order to have a good Ohmic contact between the polysilicon and the metal, any oxide that has formed at the exposed polysilicon surface should be removed. An HF dip (10:1 dilution, 5 s) after photoresist development is used to remove the native oxide on the polysilicon. After rinsing and drying the wafers, they should be loaded as soon as possible into the evaporator (Thermionics VE-100) to minimize further exposure to air. The evaporator should be loaded with titanium and platinum targets so that sequential evaporation can be done without venting and pumping the chamber. Once the chamber has been loaded and pumped to  $2 \times 10^{-6}$  Torr, evaporation of 10 nm titanium and 90 nm platinum is done. For lift-off, spraying the wafer with acetone is best because the photoresist comes off very quickly. Sonication is not recommended because it causes the lifted-off metal film to break into small pieces that can adhere to the wafer surface and become very difficult to remove. The quality of the microheater contacts is evaluated with the probe station before proceeding with the back-side etch steps.



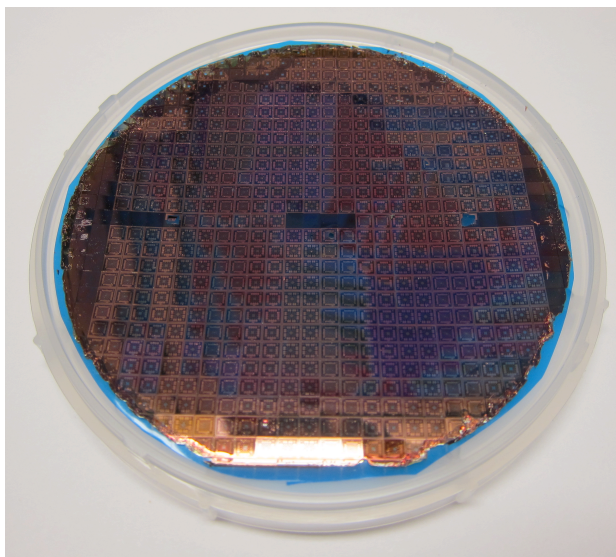
**Figure 2.** Fabrication process summary for the polysilicon microheaters. (a) Deposition of silicon nitride and doped polysilicon layers. (b) Etching of polysilicon to define the microheaters. (c) Deposition of another silicon nitride layer to encapsulate the heaters. (d) Etching of windows into the top nitride layer to allow for heater contact. (e) Metal evaporation and lift-off to form Ti/Pt heater contacts and sensing electrodes. (f) Etching of windows on backside of wafer to expose the silicon substrate. (g) Frontside coating with a KOH protective film. (h) KOH etch through the wafer to release the membrane.

The membrane release step begins with the fourth mask to open windows to the silicon substrate on the backside of the wafer (Figure 2f). Care should be taken when cleaning the wafers because the metal films are not allowed in many Nanolab tools. An acetone, isopropanol, and water rinse and dry can be used as a cleaning step here. The backside of the wafer is coated with positive i-line photoresist as with masks 1 and 2, and contact exposure is done with *ksaligner* in back-side alignment mode. The mask is aligned with no wafer loaded and an image of the mask is saved before loading the wafer with the back-side facing the mask. The front-side of the wafer is aligned with the saved mask image, since the alignment marks from the previous steps are on the front-side. After development, the wafers are plasma etched to remove the multiple layers on the back (silicon nitride, polysilicon, silicon nitride). In this case, over-etch is not as critical, because the silicon substrate will be etched anyway.

The photoresist is stripped away and the front-side of the wafer is coated with an alkaline resistant coating called Protek B3 (Figure 2g). The Protek B3 (Brewer Science) has two components. The primer layer is spun on at 1500 rpm for 60 s with a  $5000 \text{ rpm s}^{-1}$  ramp rate and then baked at  $205^\circ\text{C}$  for 60 s. Then the alkaline resistant layer is spun on at 2000 rpm for 60 s with a  $5000 \text{ rpm s}^{-1}$  ramp rate and baked at  $120^\circ\text{C}$  for 120 s and then  $205^\circ\text{C}$  for 60 s. The wafers are immersed in a 24% KOH bath at  $80^\circ\text{C}$ , with oxygen bubbling through it. Preparing the bath requires a 3 kg bottle of KOH pellets, 12.5 L of de-ionized water, and pre-heating to bring the mixture from room temperature to  $80^\circ\text{C}$ . The etch rate is approximately  $80 \mu\text{m/hr}$ , so to etch through the  $525 \mu\text{m}$  wafer takes 6.5 – 7 hrs. During this time, the water level of the bath should be checked and additional water added to maintain the proper level, otherwise the concentration of KOH will be increasing during the etch. The integrity of the Protek B3 layer should also be checked. The agitation from the oxygen bubbling and hydrogen gas released during the silicon etch can cause the Protek B3 coating to lift up at the edges, so the KOH can attack the front side of the wafer and severely damage the heater contacts. From experience, the wafers should be removed, rinsed, stripped, and re-coated approximately every 2 hours. Some devices at the wafer edge may still be affected. The KOH etch is anisotropic with angled sidewalls [71], so the membrane area is smaller than the backside window. The etch is complete when the microheaters can be seen from the back-side of the wafer (Figure 2h). Because silicon nitride is optically transparent, while silicon is not, the etch is complete when the microheaters can be seen from the back-side.

After removing the wafers from the etch bath, rinsing, and drying them, another photoresist layer (Rohm Haas SPR 220, 1500 rpm for 30 s, bake at  $90^\circ\text{C}$  for 60 s) is added on top of the Protek B3 coating for additional thickness before wafer dicing. The protective layer is important to maintain the integrity of the membrane during this process and to protect the wafer surface from small pieces of silicon generated during dicing. Wafer dicing is done with *disco*, a semi-automated dicing saw. Given the small die size ( $3.5 \text{ mm} \times 3.5 \text{ mm}$ ), it is important to make sure the wafer is securely adhered to the dicing tape and to set the blade height such that the cut leaves a small amount of the wafer connected. Otherwise, it is possible for chips to come off of the tape and hit the rotating diamond-edged saw blade, causing a lot of damage. After dicing, the photoresist layer is left on until the individual chip is ready to be used, to keep the surface free of dust. Figure 3 shows an optical image of one processed wafer. Each chip is cleaned with acetone,

isopropanol, DI water, and dried with nitrogen before characterization or sensing material deposition. For sensor operation, each chip is wire-bonded in an 8 or 14-pin ceramic dip package using Al-1% Si wire and a silver epoxy to hold the chip in place on the package. The silver epoxy must be applied carefully such that it does not fill the cavity in the back of the chip and provide a heat sink to the package. This way the thermal isolation of the microheater can be maintained.



**Figure 3.** Optical image of one processed wafer with a couple hundred microheater chips.

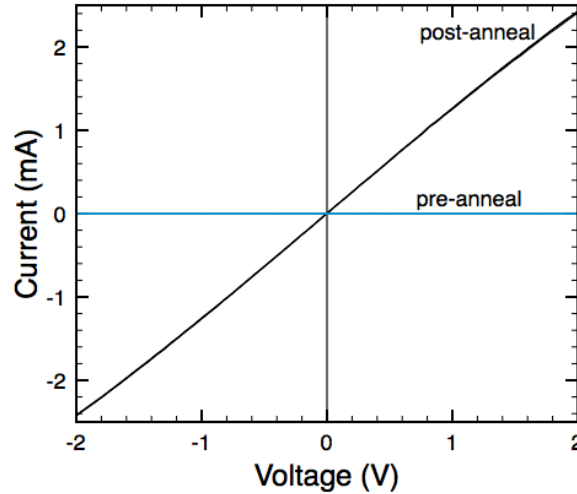
## 4. Characterization of the polysilicon microheater

### 4.a. Electrical characterization

Ideally, the polysilicon microheaters should exhibit a linear current-voltage relationship, such that there is no significant barrier between the metal contact layer and the polysilicon. After the metallization, the microheater resistance is high, as seen in Figure 4 as the pre-anneal line. Driving current through the microheater results in a resistance decrease. After the application of a 5 V potential across the microheater for at least 30 s or scanning the potential between -5 and 5 V several times, the resistance drops from several  $M\Omega$  to 1-2  $k\Omega$  and a linear current-voltage relationship is observed (Figure 4, post-anneal). Several explanations are possible, such as tunneling through a thin oxide layer between the titanium and polysilicon layers [72] or formation of titanium silicide at the contact interface. If the contact has a high resistance before annealing, then Joule heating at the contact interface may raise the temperature and promote the silicidation [73]. It is also possible that the current-induced resistance drop occurs in the polysilicon layer rather than the contact. Joule heating at the grain boundaries in the polysilicon may result in irreversible local melting and dopant segregation [74], [75]. In any case, after the initial anneal, the microheater has the desired linear current-voltage relationship.

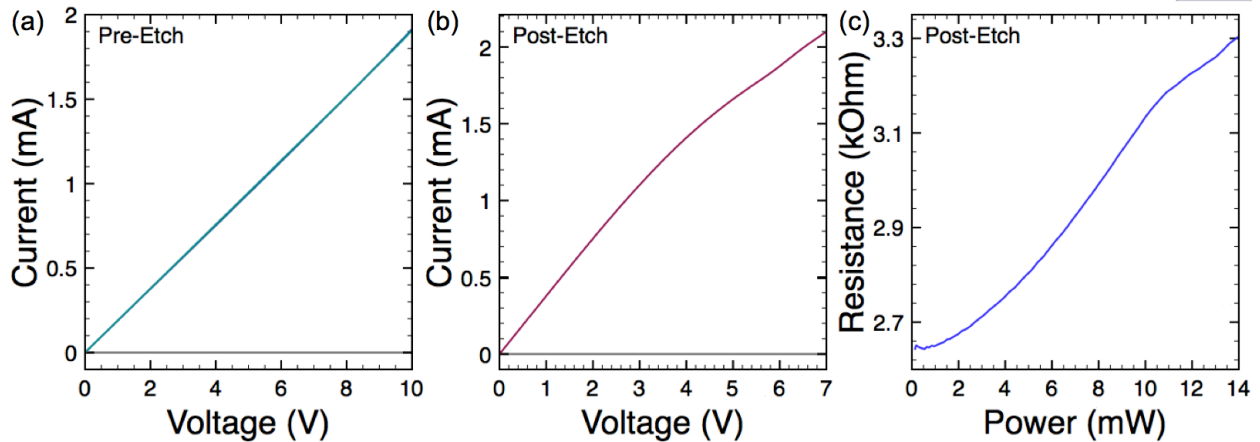
The heater resistance is measured during characterization and sensor operation using a two-point measurement. The heater resistance is high enough ( $\sim 2\text{ k}\Omega$ ), that the contribution from the leads is negligible and a four-point measurement is unnecessary. Because of variation in the film

thicknesses and doping level across the wafer, the heater resistances vary by 15% across a wafer. This necessitates characterization and calibration of each microheater before use.



**Figure 4.** Representative current-voltage curve of one microheater before and after anneal.

Before the microheater chips are back-etched to release the membrane, they exhibit linear I-V behavior across a wide range of potentials. After etching, the heater elements are thermally isolated and as the applied potential is increased, the temperature of the heater increases through Joule heating. For polysilicon, the elevated temperature results in a higher resistance and thus a lower current for a given potential. Figure 5a shows the linear I-V up to 10 V applied potential for a pre-etch (unreleased) microheater chip, while Figure 5b shows the current of a post-etch (released) microheater decreasing at higher applied potential. The post-etch devices are shown with a smaller potential window because the membrane will crack at applied potentials higher than 7.5 V due to the induced thermal stress.



**Figure 5.** (a) Linear I-V for unreleased microheater (pre KOH-etch step) up to 10 V applied potential. (b) Released microheater (post KOH-etch step) showing decreasing current as applied potential is increased. (c) Resistance versus applied power for released microheater as calculated from the I-V information in (b).

The current vs. voltage curve in Figure 5b is used to calculate the power ( $P = I \cdot V$ ) and resistance ( $R = V/I$ ), and the resulting power-resistance curve is plotted in Figure 5c. The resistance increases with applied power, giving a positive temperature coefficient of resistance (TCR). The sign of the microheater TCR is controlled by the competing effects of increased phonon scattering in the crystal grain leading to an increasing resistance with temperature, and thermal activation of carriers through the grain interfaces leading to a decreasing resistance with temperature [21], [76]. The change in slope observed in Figure 5c at 10 mW coincides with the recrystallization temperature of polysilicon [77], [78].

#### 4.b. Temperature calibration

The microheater temperature is determined by balancing the heat generated through Joule heating and the heat lost through various heat transfer modes [79]. The heat generated through Joule heating is equivalent to the applied power. Heat transfer can occur through conduction to the substrate, conduction to the air, and radiation. Convection through the air is minimized with the sensor packaging and the small size of the heated element. Modeling conduction with Fourier's law gives a linear relationship between applied power and the temperature difference between the microheater and room temperature:

$$P = -kA \nabla T \quad (2)$$

where  $P$  is the transferred heat,  $k$  is the thermal conductivity of the material the heat is transferring through,  $A$  is the area and  $\nabla T$  is the temperature gradient. There are two conduction components, through the air and through the membrane. The microheater shape is complex to model without relying on computation, but it can be roughly approximated as a thin cylinder where there is conduction to the air in the  $z$ -direction and conduction through the membrane in the  $r$ -direction. In both cases, regardless of the geometric factors, the transferred heat is directly proportional to the temperature difference between the ambient and heater temperature,  $\Delta T$ . Given the low thermal conductivity of air ( $26.2 \text{ mW m}^{-1} \text{ K}^{-1}$ ) and silicon nitride ( $1000 \text{ mW m}^{-1} \text{ K}^{-1}$ ) [62], it can be assumed the temperature drops off rapidly from the hot zone of the microheater, such that the derivative of temperature with distance can be replaced with  $\Delta T$  divided by the relevant distance.

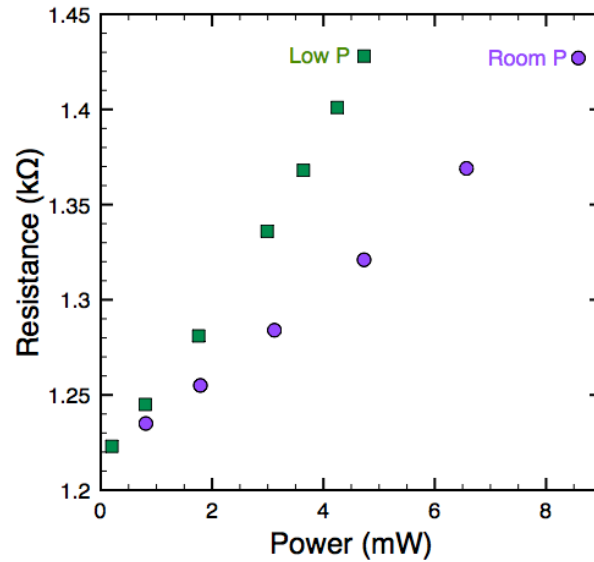
Radiation modeled based on the Stefan-Boltzmann law of blackbody radiation follows a highly non-linear equation:

$$P = A \sigma \epsilon \Delta T^4 \quad (3)$$

where  $\sigma$  is the Stefan-Boltzmann constant,  $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ . Assuming an emissivity,  $\epsilon$ , of 1 and a hot area,  $A$ , of  $50 \times 50 \text{ } \mu\text{m}^2$ , the radiative power only reaches  $\sim 0.1 \text{ mW}$  at  $700 \text{ }^\circ\text{C}$ , which is less than 1% of the total applied power. Therefore, in the operating temperature range of the microheater, radiative effects can be considered to be negligible. This leaves an applied power relationship that is linear with the temperature difference and dependent on the thermal conductivity of the air and the membrane and heater materials, as well as the heater geometry.

The relative impact of conduction to the substrate versus the air is studied by placing the microheater inside a vacuum chamber. At room pressure and temperature, the microheater requires  $8.6 \text{ mW}$  applied power to reach a resistance value of  $1.427 \text{ k}\Omega$  (Figure 6). At room

temperature and low pressure (50 mTorr), the microheater only needs 4.7 mW to reach the same resistance. The thermal conductivity of air at 50 mTorr pressure is 300 times lower than air at 1 atm, thus the heat lost through conduction decreases by the same amount [80]. Assuming that the resistance at a given temperature remains constant, this indicates that at room pressure, 55% of the heat is lost through conduction to the air and 45% through conduction to the substrate.



**Figure 6.** The resistance versus power for a polysilicon microheater at room temperature under atmospheric pressure conditions and low pressure (50 mTorr) conditions.

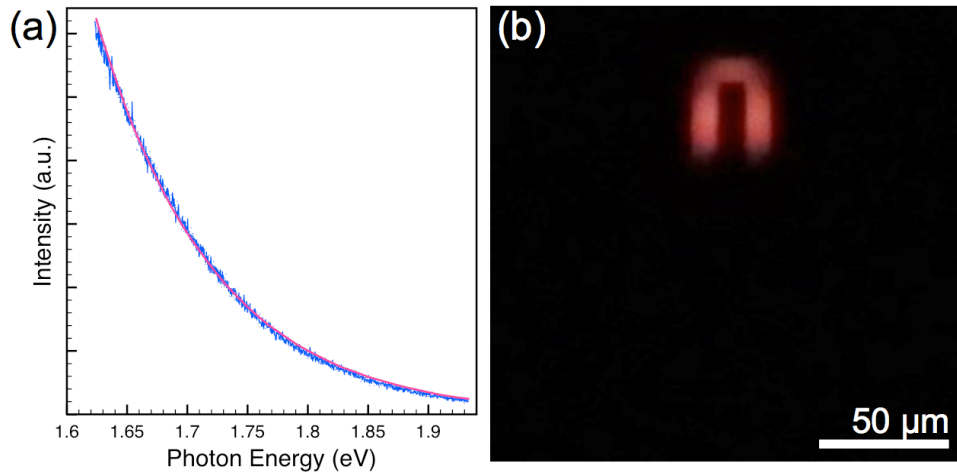
Considering that the applied power is linearly proportionally to the temperature difference between the microheater and the surrounding air, a calibration curve can be constructed with two points: zero power for the microheater at room temperature and one other point with the microheater at elevated temperature. One calibration method measures the radiation output of a microheater when it is heated to the point where it visibly glows. The emitted spectrum over a range of wavelengths is collected using a spectrometer with a small spot area. An estimated temperature is obtained by fitting the emitted spectrum to a Planck distribution:

$$B_v(\nu, T) = 2h\nu^3 c^{-2} [\exp(h\nu/k_b T) - 1]^{-1} \quad (4)$$

where  $B_v$  is the spectral radiance,  $h$  is the Planck constant,  $k_b$  is the Boltzmann constant,  $c$  is the speed of light in air, and  $\nu$  is the frequency. In previous work, this technique gave good agreement with a platinum resistive temperature detector (RTD) integrated with the microheater [79]. Figure 7a shows the recorded emission spectrum for a microheater and the Planck radiation fit that is used to calculate the temperature. The applied power to reach an approximate temperature of 700 °C (or onset of glow) is  $18 \pm 1$  mW for the polysilicon microheaters.

Another common technique for temperature calibration is through thermal equilibration of the entire microheater chip. The microheater can be placed inside a furnace or heated chamber and the resistance measured at a series of temperatures after the furnace temperature has equilibrated. This type of calibration assumes that the microheater resistance is dominated by the segment that

is heated in actual operation (leads are neglected). However, the microheater design used here has long sections of polysilicon running from the U-shape of the microheater to the substrate, where the electrical contact is made. The contribution of these to the overall resistance is not negligible. If the entire microheater chip is heated, then all of the polysilicon is at the same high temperature. But with an applied potential across the microheater, the narrowest part of the polysilicon trace is much hotter than the rest. Figure 7b shows one microheater element powered to glowing where it is evident when compared to Figure 1c that the narrowest part of the polysilicon trace is the place where the most heat is dissipated. Because the polysilicon resistance increases with temperature, the microheater resistance should be lower in the case where only the narrowest portion is at temperature, compared to where the entire chip is heated to that temperature. Experimentation confirms this with a microheater resistance of 1.5 k $\Omega$  when the applied power should give a temperature of 250 °C compared to a resistance of 1.67 k $\Omega$  when the entire chip is heated to 250 °C in a furnace.



**Figure 7.** (a) Radiation spectrum (blue) and Planck distribution fit (red) for a microheater powered to the glowing point. (b) Optical image of one microheater element powered to the glowing point, showing the localized heated area.

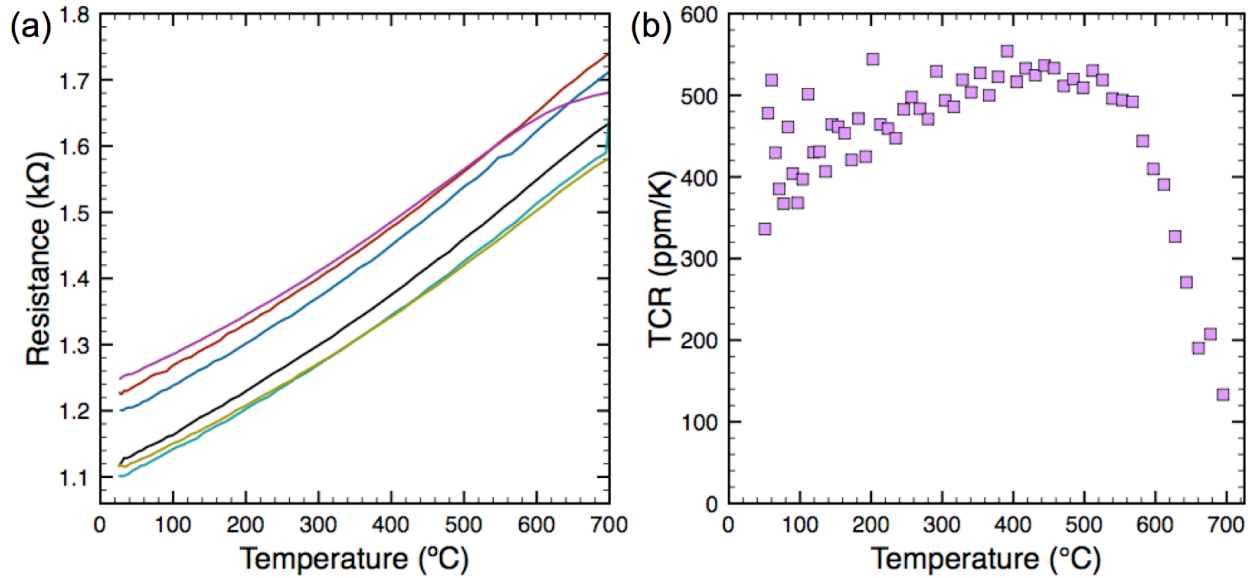
With the temperature calibration complete, Figure 8a shows the resistance versus temperature relationship for several microheater devices from the same wafer. The temperature coefficient of resistance ( $\alpha$ ), defined as:

$$\alpha = (R - R_0) / R_0 \cdot \Delta T \quad (5)$$

can be calculated for the range between 300 and 500 °C from the slope and the resistance value at 300 °C. The TCR of the polysilicon microheaters is 614 ppm K<sup>-1</sup> on average with a standard deviation of 27, which is comparable with prior reports for highly doped n-type polysilicon [28], [76], [81]–[83]. Figure 8b shows the change in TCR for one polysilicon microheater over a range of temperatures. It can be seen that above 500 °C, the TCR starts to decrease sharply, which affects the sensitivity of catalytic gas detection in this operating temperature range. Prior reports have shown that the magnitude and direction of the TCR of polysilicon is heavily impacted by doping level and grain size [76], [81], with negative TCR values observed at low doping levels.



Because of variation in deposition across a wafer and from batch to batch, the TCR and the applied voltage required to reach the desired power levels are determined for each individual microheater chip. Additionally, it is lower than typical values for platinum (1500-2200 ppm K<sup>-1</sup> [20]). However, the reliability issues of platinum, including electro-migration, oxidation, and poor adhesion, make polysilicon a better choice of heater material, as discussed in Chapter 1.



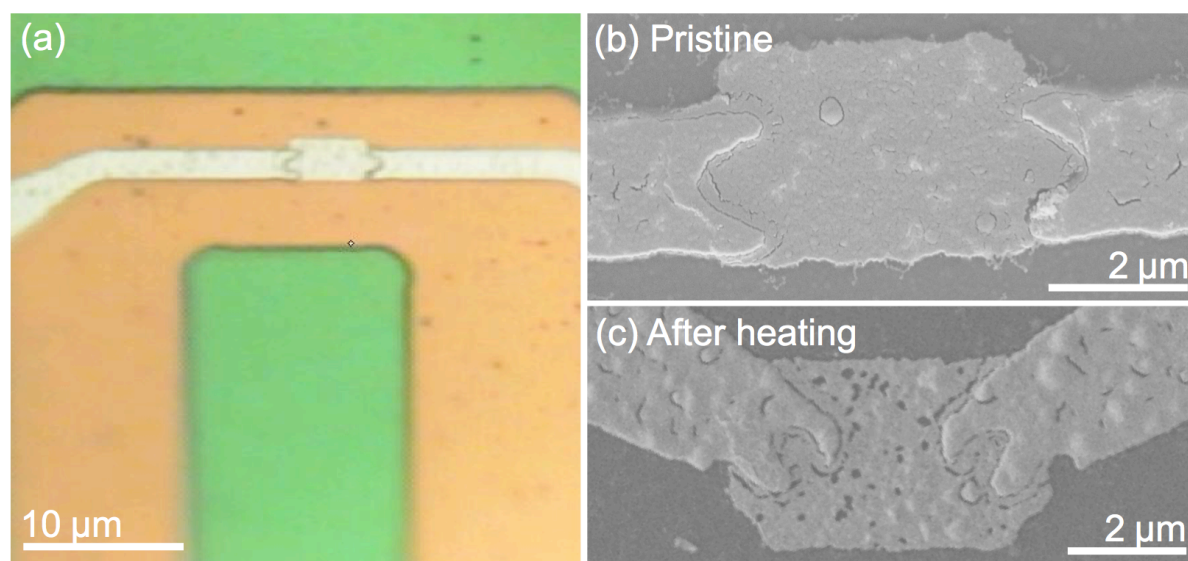
**Figure 8.** (a) Resistance versus temperature relationship for several polysilicon microheaters. (b) Temperature coefficient of resistance versus temperature relationship for the polysilicon trace shown in pink in part (a).

A prior version of the polysilicon microheater based on a bridge structure found the thermal time constant to be  $\sim 50 \mu\text{s}$  [79]. With the closed membrane, the thermal capacitance of this microheater design is larger, which would lead to a longer thermal time constant, but based on other works with similar heater materials and membrane geometry [15], [62], [82], [84], the thermal time constant of the closed-membrane microheater is on the order of 1 ms.

## 5. Temperature Sensing

One method to further increase the utility of the microheater platform is to split the heating and temperature sensing functions, such that the materials can be independently optimized. With a separate temperature sensor, the heater could also be operated with a closed loop to maintain the operating temperature even with drift. A preliminary attempt to introduce a separate temperature sensor element was made using a thin (20 nm) evaporated patch of platinum to connect the existing sensing electrodes (Figure 9a). Platinum is commonly used for resistive temperature detection and the thin patch (with higher resistance than the 100 nm thick leads) located directly above the microheater ensures that the hottest temperature is measured. During testing, a few negative features were observed with this fabrication. The platinum trace had a higher resistance than was estimated, possibly due to poor contact between the thin layer and the 100 nm sensing electrodes. It is possible to achieve the same effect of having a high resistance area at the center of the microheater by changing the width of the trace and performing the fabrication with only

one evaporation step. However, more critically, the platinum trace suffered from adhesion problems during high temperature operation of the heater. In Figure 9b and c, a scanning electron microscopy image of the trace is shown before and after heating to 500 °C, where voids can be seen in the heated film. The consequence of this instability is that the resistance of the trace increased from 500 to 2000  $\Omega$  and the noise level increased dramatically, leaving it unable to distinguish between temperatures in the range of interest. Further development will have to take into account the stability of the temperature sensor material at high temperature. For platinum, there are adhesion layers that can improve the high temperature stability [61], [85], [86], but other materials are also possible candidates. Research efforts in microbolometer fabrication have identified vanadium dioxide as a material with a very high TCR (25,000 ppm K<sup>-1</sup> [87]), which could give a high sensitivity for combustible gas detection and a low detection limit.



**Figure 9.** (a) Optical image showing placement of platinum trace on microheater. (b,c) SEM image of platinum film (b) before and (c) after heating to 500 °C, showing void formation.

## 6. Conclusion

A low-power polysilicon microheater has been designed, fabricated, and characterized for use as a sensor platform. Design features include a suspended heater to reduce the power loss to the substrate, a closed membrane for ease of sensing material deposition, a small heated area to minimize power consumption, metal contacts placed off the membrane for increased contact stability, and sufficient space between the sensing and heater electrodes to minimize potential for shorting. Polysilicon is chosen as the heater material due to its tunable resistivity and resistance to electromigration. Low stress silicon nitride encapsulates the polysilicon microheater into a thin membrane that provides thermal isolation from the substrate. Low-resistance contact can be made to the microheater using a platinum/titanium metallization scheme. The resulting microheaters require only 18 mW to reach 700 °C and have linear temperature coefficients of resistance in the operating range of 200-500 °C. The microheater platform is versatile in that it can be used for both conductometric and calorimetric sensing.

## Chapter 3. Platinum Nanoparticle-Loaded Graphene Aerogel for Hydrogen Sensing<sup>2</sup>

### 1. Motivation

Hydrogen is an important industrial gas used in a variety of applications, and has become especially popular as an alternative fuel for transportation. As hydrogen is odorless, colorless, and flammable, it is critical to install hydrogen gas monitoring systems that can detect potentially explosive situations [88]. Hydrogen has a lower explosive limit of 4% or 40,000 ppm, which is the minimum concentration required for ignition [88]. Detection technologies should give warning well before this limit is reached (often the alarm set point is 2-10% of LEL). Several different sensing schemes exploiting various chemical properties of hydrogen have come under consideration and development [89], including catalytic combustion sensors [9], [19], thermal conductivity sensors [90], [91], electrochemical sensors [92], [93], semiconducting metal-oxide sensors [94], and metallic resistors [95], [96].

Catalytic combustion sensors are widely used in industry. However, the catalyst must be heated to high temperature in order to promote hydrogen combustion, resulting in relatively high power consumption. These sensors consist of a Joule-heated platinum wire coated with a catalyst-containing support material, typically a ceramic. The catalyst promotes combustion, generating heat, causing the temperature of the Pt wire to increase. This increase in temperature causes an increase in the resistance of the Pt wire. This change in resistance is typically measured using a Wheatstone bridge configuration with a reference element that is identical minus the catalyst to offset atmospheric changes in temperature or humidity. While these sensors are widely deployed, their relatively high level of power consumption has impeded their implementation as long-term, battery-powered monitors. Advances in MEMS technology have allowed for decreased power consumption through device miniaturization [9], [97]. For a typical MEMS catalytic combustion sensor, a microfabricated Pt or polysilicon heating element, or microheater, is embedded in a thin silicon nitride membrane upon which a catalyst layer is deposited. Due to scaling laws, the drastic reduction in size of the microheater provides a corresponding reduction in thermal response time. The short thermal response time allows for rapid heating and cooling of the device, thereby enabling low duty cycle operation and further reduction in power consumption.

Many of the reported microheater-based hydrogen gas sensors use a catalyst layer of Pt or Pd nanoparticles dispersed in a porous alumina or silica support [19], [98], [99]. Recent work by Brauns, et al. employ Pt nanoparticles stabilized with surfactant molecules eliminating the need for a porous ceramic support, thereby reducing the thermal mass (hence lowering the power consumption) and transferring heat more efficiently (leading to higher sensitivity and faster response time) [25]–[27]. However, due to the thermal instability of the surfactant, these sensors are not amenable to high temperature application or operation.

---

<sup>2</sup> A modified version of this work was published in A. Harley-Trochimczyk, J. Chang, Q. Zhou, J. Dong, T. Pham, M. A. Worsley, R. Maboudian, A. Zettl, and W. Mickelson, “Catalytic hydrogen sensing using microheater platinum nanoparticle-loaded graphene aerogel,” *Sensors and Actuators B: Chemical*, vol. 206, pp. 399-406, 2015.

Here we report the fabrication and characterization of a catalytic hydrogen sensor using platinum (Pt) nanoparticle catalyst embedded in graphene aerogel catalyst support. Aerogel is a porous material derived from a gel in which the liquid component of the gel is replaced with a gas phase. The Pt nanoparticle-loaded graphene aerogel is deposited on a low-power polysilicon microheater device, which is used to both heat the catalyst and detect the heat output from the catalytic combustion of hydrogen. The synthesis and characterization of the graphene aerogel and platinum functionalization is described. The measurement of this catalytic hydrogen sensor is described and optimized for sensitivity, selectivity, and stability.

## 2. Material synthesis and characterization

Graphene aerogel is chosen as the catalyst support since it provides a high surface area ( $>1000 \text{ m}^2 \text{ g}^{-1}$ ) [100] onto which a catalyst material can be deposited, a high in-plane thermal conductivity ( $\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$  in-plane for graphene [101]) to efficiently transfer heat to the microheater, and is also stable below  $500^\circ \text{C}$  [100], enabling high temperature operation. Platinum nanoparticles are chosen as the catalyst material, due to their well-established catalytic properties and high surface area. Embedding platinum nanoparticles into the graphene aerogel provides a highly catalytically active material, which can transfer heat with minimal additional mass and is stable at elevated temperatures.

### 2.a. Graphene aerogel

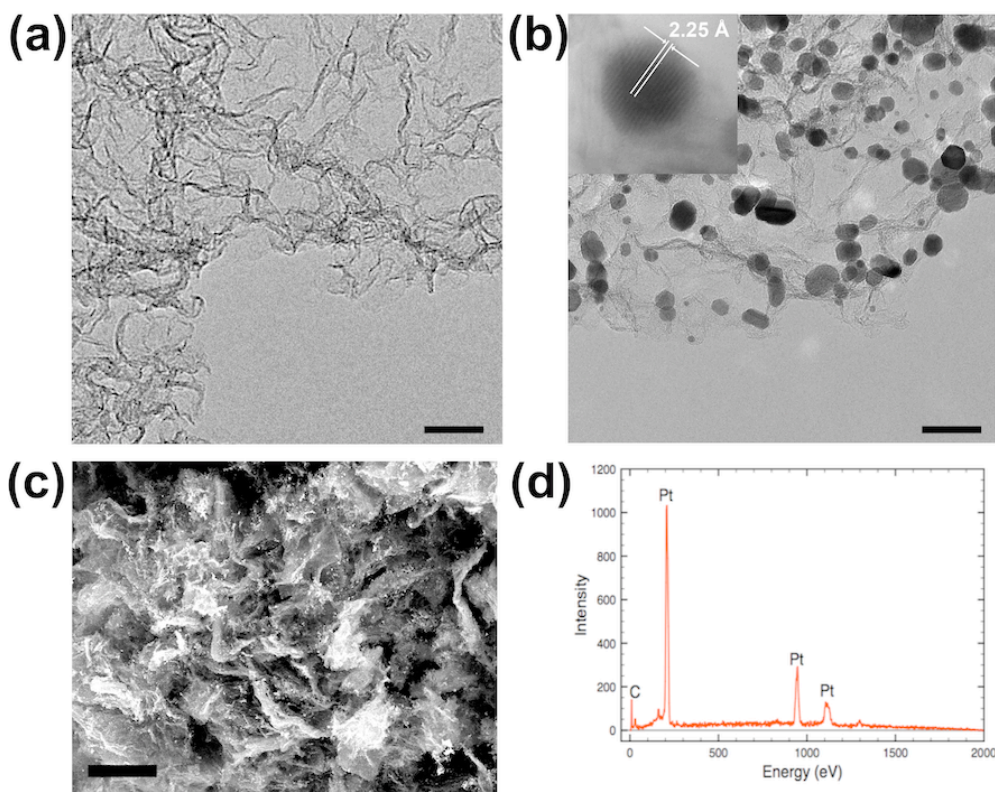
Graphene aerogel (GA) is prepared using the method in Ref. [102]. A precursor of graphene oxide (GO) is prepared with Hummer's method [103]. The chemical functionality of the GO sheets is used to cross-link the sheets. The graphene oxide is dispersed in deionized water at 1-2 wt%. Concentrated ammonium hydroxide is added to the GO suspension and cured in a sealed glass vial at  $85^\circ \text{C}$  for 12 h. The gel is washed with deionized water to remove remaining  $\text{NH}_4\text{OH}$  and then the water is exchanged with acetone before drying with supercritical  $\text{CO}_2$ . After supercritical drying, carbonization is achieved through pyrolysis at  $1050^\circ \text{C}$  under nitrogen.

Typical graphene aerogel density is  $80\text{-}100 \text{ mg cm}^{-3}$  with Brunauer-Emmett-Teller (BET) surface areas  $>1000 \text{ m}^2 \text{ g}^{-1}$ , as calculated with nitrogen adsorption [104]. The pore size distribution, determined with the Barrett-Joyner-Halenda method [105], is largely between 3 and 10 nm with a peak at 6 nm [102], which suggests that most of the surface area will be accessible to hydrogen gas molecules. Variation in the pyrolysis temperature affects the crystallinity and thermal stability of the graphene aerogel, as reported in [100]. For GA pyrolyzed at  $1050^\circ \text{C}$ , there is a weight loss of 10% when heated to  $500^\circ \text{C}$ , with a 50% drop by  $575^\circ \text{C}$ . Because the GA will be heated in sensor operation, care must be taken that temperatures remain in stable range. The aerogel is extensively analyzed by several methods, including transmission electron microscopy (JEOL 2010). A representative TEM image of as-synthesized graphene aerogel is shown in Figure 1a, showing few-layer wrinkled sheets. The electrical conductivity of the bulk aerogel is  $100 \text{ S m}^{-1}$ , as determined through the four-probe method [102]. The graphene assembly also has a high degree of mechanical stability with a Young's modulus of  $\sim 50 \text{ MPa}$  [102]. The mechanical stability is important because it allows the pyrolyzed aerogel to be suspended in liquid and dried without collapsing the pores.

### 2.b. Platinum nanoparticle-loaded graphene aerogel

To decorate with Pt nanoparticles, the graphene aerogel is submerged in a solution of chloroplatinic acid in ethanol. The aerogel is then transferred into deionized water and freeze dried to ensure even distribution of the platinum salt. Finally, the platinum salts are reduced to platinum metal by heating under hydrogen gas at 450 °C [106]. The loading and size of the Pt nanoparticles deposited on the graphene aerogel is confirmed with transmission electron microscopy and scanning electron microscopy (SEM, FEI Sirion XL30). Energy dispersive x-ray spectroscopy (EDAX) is used for elemental analysis.

Figure 1b shows a TEM image of graphene aerogel that has been loaded with platinum nanoparticles. The average nanoparticle size is 6.3 nm  $\pm$  3.3 nm, as determined by analysis of several TEM images. The nanoparticles are crystalline, as shown in the inset of Figure 1b, and display a lattice spacing of 2.25 Å, consistent with the platinum (111) crystal planes. Figure 1c shows an SEM image of the Pt NP-loaded graphene aerogel confirming a uniform loading of platinum nanoparticles throughout the material. Energy dispersive x-ray spectroscopy confirms that only carbon and Pt are present, as shown in Figure 1d.



**Figure 1.** (a) TEM image of graphene aerogel prior to loading with platinum nanoparticles. (b) TEM image of Pt nanoparticles dispersed on the graphene aerogel. Dark nanoparticles are supported on the lower-contrast nanoporous graphitic structure. (b, inset) TEM showing Pt (111) spacing of 2.25 Å. (c) SEM shows Pt loading over a large area, including some larger clusters. (d) EDAX spectra confirming carbon and platinum are the only elements present. Scale bars: (a,b) 20 nm; (c) 5  $\mu$ m

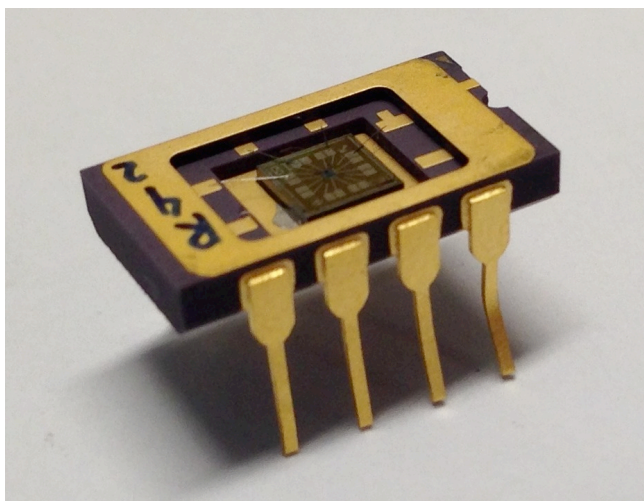


### 3. Device fabrication and test methods

The polysilicon microheater is fabricated as described in Chapter 2, diced, and wire-bonded into an 8- or 14-pin ceramic dual in-line package (CerDIP), as shown in Figure 2.

#### 3.a. Integration of sensing material on microheater

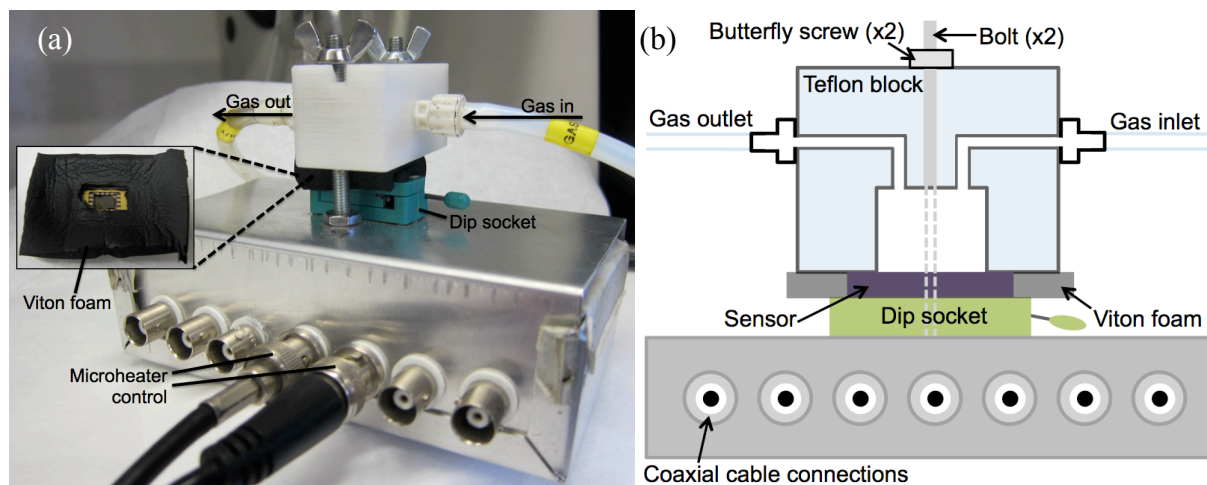
The platinum nanoparticle-loaded graphene aerogel material is sonicated into suspension and deposited from a solution of isopropyl alcohol. A 0.25  $\mu\text{L}$  drop of 0.5 mg/mL solution is placed on the microheater chip while the microheater is powered to 8 mW ( $\sim 220^\circ\text{C}$ ). Heating the microheater promotes solvent evaporation and leads to material deposition at the center of the microheater. The microheater heated at 8 mW for 3 hours to ensure all the solvent is evaporated.



**Figure 2.** Individual microheater chip wire-bonded into a ceramic dual in-line package.

#### 3.b. Sensor measurements and gas delivery

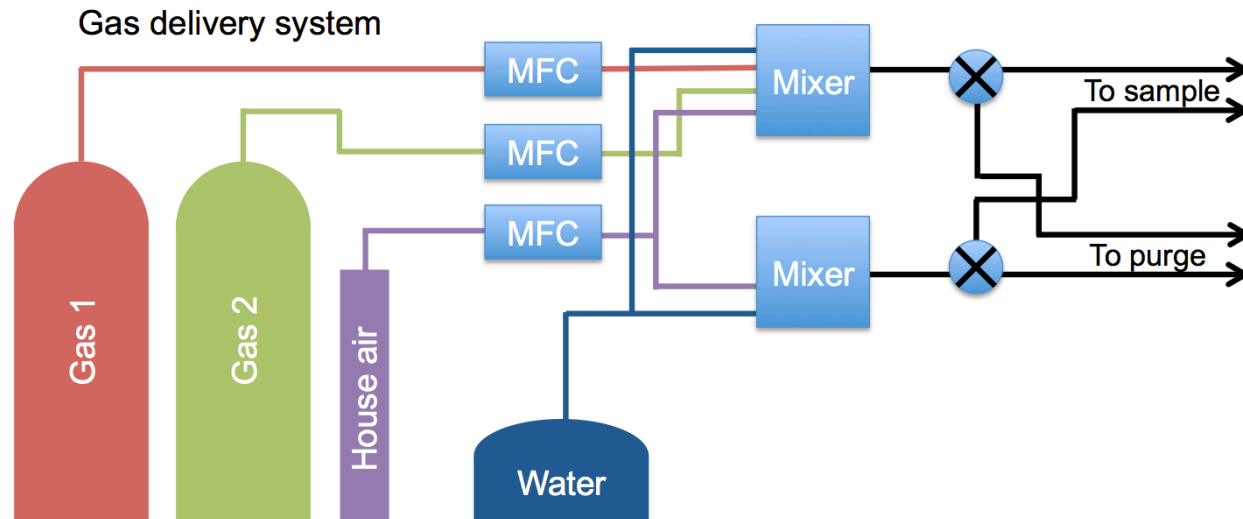
The microheater CerDIP package is placed within a gas flow chamber (Figure 3a) with a volume of 1  $\text{cm}^3$ . The chamber is made of Teflon with two channels for gas inlet and outlet flow and a 1  $\text{cm}^3$  cavity drilled into it, as shown in the schematic in Figure 3b. The gas lines are also Teflon, to prevent adsorption and accumulation of gases. The sensor package (seen in Figure 2) fits into a green DIP socket (3M) that is electrically connected through a bud box to 14 co-axial cable outlets. The microheater is then controlled by connecting the leads from the Keithley 2602A source-meter to the outlets on the bud box that correspond to the correct pins. A piece of Viton foam is used to seal the gap between the DIP socket and the Teflon gas chamber block. The inset in Figure 3a shows an image from the top of the packaged microheater with the Viton foam showing that the foam has a cut out to allow for direct gas flow. The butterfly screws on top of the Teflon block maintain the chamber seal.



**Figure 3.** (a) Optical image of gas testing chamber with gas inlet and outlet and microheater controls. Inset shows the top view if the Teflon gas chamber is lifted off. (b) Schematic diagram of gas testing chamber.

The sensor is exposed to target gases using a computer-controlled gas delivery system, shown in Figure 4. Two target gas tanks can be connected at one time. Stream balance and purge is made up of house air that has passed through pressure swing adsorption dryers to remove humidity and an activated carbon scrubber to remove other contaminants. A tank with liquid water is used to humidify streams on demand by evaporating the water and mixing it with the gases. Mass flow controllers (Bronkhorst) controlled by LabView are used to deliver the correct amounts of each gas to the streams. Labview also controls the valves that can send the mixed gas stream to the sensor chamber (where the sample is) or to be vented in the fume hood (purge).

For this work, a cylinder of 3% hydrogen gas balanced in nitrogen is used (Praxair). For selectivity tests, sensors are exposed to various concentrations of diethylether (Praxair, 5000 ppm in  $N_2$ ), n-pentane (Praxair, 5000 ppm in  $N_2$ ), and methane (Praxair, 5% in  $N_2$ ) using the same gas delivery system. Sensor testing is performed at a constant flow rate of 300 sccm. Flow stream temperatures are recorded and are within a few degrees of room temperature. In most of the tests, the gas mixture from the analyte gas cylinder is mixed with clean air to attain the desired analyte concentration. In these tests, the oxygen concentration in the gas stream is at least 12 times the stoichiometric concentration to oxidize the hydrogen to form water. The exceptions are: (i) a test performed in pure nitrogen to show the lack of catalytic response in the absence of oxygen (Figure 7b); and (ii) a test to assess sensor response to various oxygen concentrations, where the desired oxygen concentration is attained by mixing the hydrogen gas with pure oxygen and nitrogen (Figure 8). In these cases, the second gas tank is pure oxygen and the house air is replaced by a pure nitrogen tank.



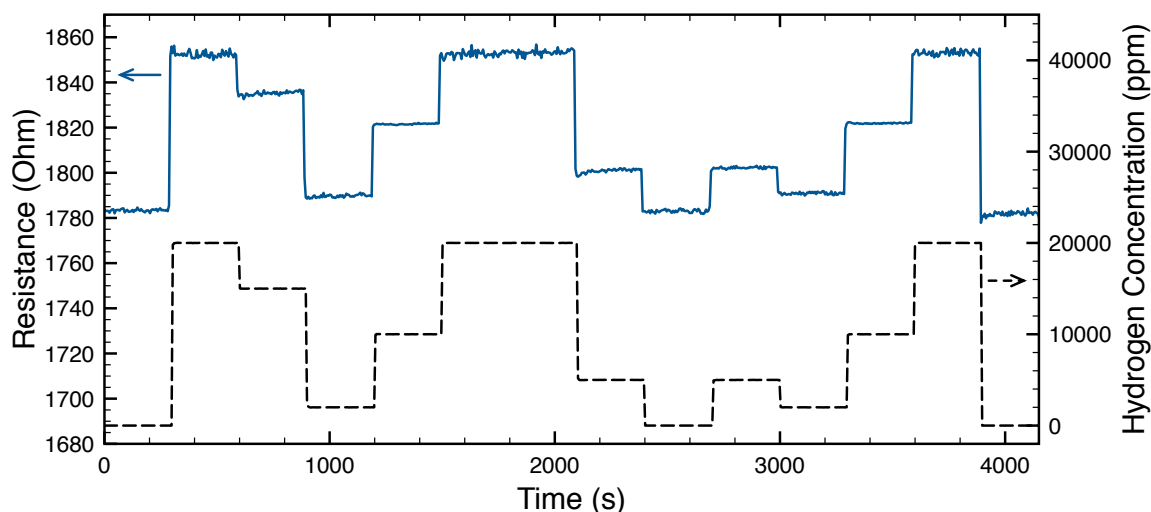
**Figure 4.** Schematic of the computer-controlled gas delivery system. Two target gases can be connected at once and are balanced with clean, dry house air. There is a liquid water source for tests with humidity, which is evaporated and mixed with the gas stream. Mass flow controllers (MFC) are used to control the flow and after the streams are mixed, there are two valves controlling whether the stream is sent to the sample or purge (vented into the fume hood).

The measurement of the microheater sensor is performed using a Keithley 2602 source-meter. The source-meter is controlled using Zephyr, an open-source Java-based instrument and control and measurement software suite. Zephyr is also used to acquire data from the source-meter, the gas delivery system, such as flow rates and concentrations, and any reference sensors, such as temperature sensors. The microheater sensors are measured either by continuously applying a bias voltage or by pulsing the heater to a particular voltage for a specified amount of time. Sequences comprised of multiple voltage pulses are used to quickly change the sensor temperature and these pulsed sequences are continually repeated after a specified period. The sensor response is determined by the relative change in resistance,  $\Delta R/R_0$ , where  $R_0$  is the average resistance during zero hydrogen exposure,  $R$  is the average resistance during exposure to a given hydrogen concentration, and  $\Delta R = R - R_0$ .

#### 4. Sensing results

The Pt NP-loaded graphene aerogel is deposited onto the microheater device to complete the fabrication of the catalytic hydrogen sensor and it is placed into the gas sensing setup for testing. The sensor is exposed to hydrogen concentrations between 0 and 20,000 ppm during which the temperature of the microheater is ramped between 25 and 430 °C. This is accomplished by applying a nine-level voltage pulse sequence with 500 ms at each voltage from 0.1 to 5.2 V. When the sensor is heated in the presence of hydrogen, the resistance increases due to heat generated from catalytically combusting the hydrogen gas on the platinum nanoparticles. Figure 5 shows the resistance of the microheater (blue) at a particular temperature level in the pulse sequence versus time as the sensor is exposed to a various concentrations of hydrogen. While data is collected for all nine levels, only the 15 mW (430 °C) is shown for clarity. A stable, reproducible response is observed during exposure to hydrogen during the 70-minute test.





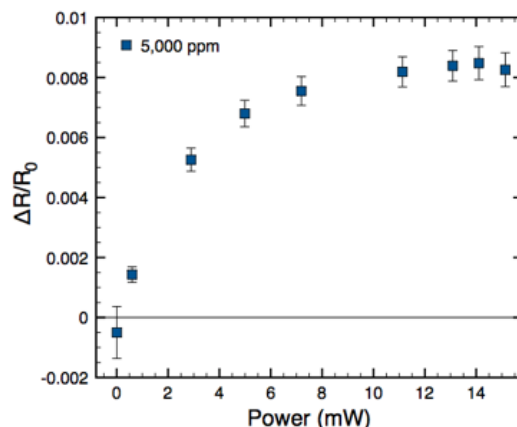
**Figure 5.** Resistance of the sensor (blue) for varying hydrogen concentration (black, dashed line) versus time for the 15 mW (430 °C) level of the nine-level pulse sequence.

To determine the optimum operation temperature for the sensor, the response, taken as  $\Delta R/R_0$ , is analyzed as a function of input power for the various hydrogen concentrations. Figure 6a shows the average sensor response to 5,000 ppm hydrogen versus power for all nine voltage levels in the pulse sequence. The sensor response increases with increasing heater power, and then plateaus above 11 mW (320 °C). Similar results are seen at other hydrogen concentrations, up to 20,000 ppm. The combustion reaction is first order in hydrogen concentration and the relationship between the reaction rate,  $k$ , and temperature can be expressed by the Arrhenius equation,

$$k = A \cdot \exp(-E_a/RT) \quad (6)$$

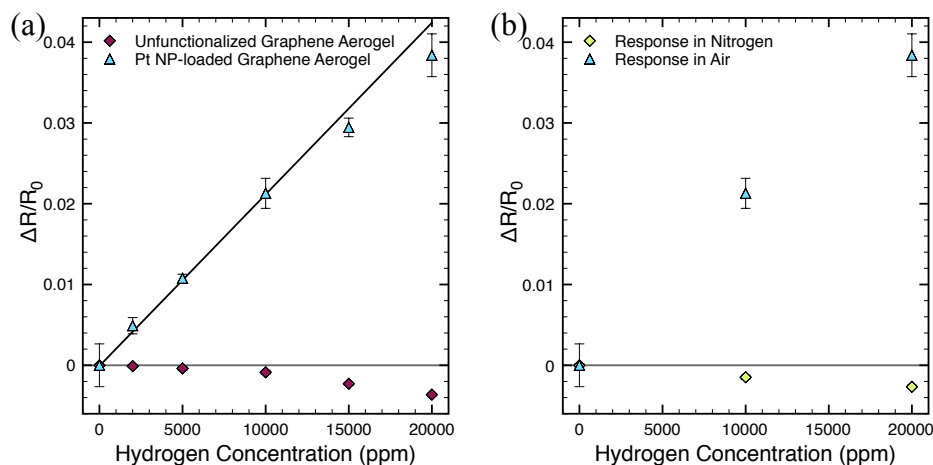
where  $R$  is the ideal gas constant,  $E_a$  is the activation energy, and  $A$  is an empirically determined pre-exponential factor. Since the reaction rate increases with temperature, if the sensitivity plateaus with increased temperature, this indicates that the sensor response is limited by the amount of gas that reaches the catalyst rather than the reaction rate. Therefore, the sensor is operating in a mass transfer limited regime. Further sensor characterization presented here is performed at 11 mW (320 °C), which balances the need for a high sensitivity and low power consumption.

Keeping the sensor at 11 mW not only decreases power consumption, but also improves catalyst support lifetime. The graphene aerogel has been shown to be stable up to 500 °C, as discussed in Section 2a. During exposure to high concentrations of hydrogen, i.e. up to 20,000 ppm, the resistance of the microheater can change by up to 4%, which would correspond to an increase of over 200 °C. Therefore, by operating the sensor at a baseline temperature of 320 °C, exposure of the sensor to temperatures above 500 °C can be minimized and the catalyst lifetime prolonged. Additionally, the resistance versus temperature relationship is linear in the range from 300 to 500 °C (Chapter 2, Figure 8), which simplifies analysis of the sensor response.



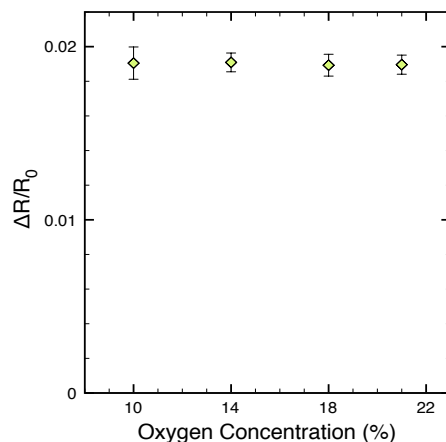
**Figure 6.** Fraction change in sensor resistance versus power during 5,000 ppm hydrogen exposure. The error bars represent the standard deviation of the response over the test duration.

Figure 7 shows the response of a microheater sensor that has been functionalized with the Pt NP-loaded graphene aerogel (blue, triangles) and with a bare unfunctionalized graphene aerogel (burgundy, diamonds). The response of the Pt NP-loaded graphene aerogel sensor shows a nearly linear, positive dependence on hydrogen concentration, whereas the unfunctionalized graphene aerogel sensor shows only a slight negative response. This negative response is due to the increase in thermal conductivity of the flow stream with increased hydrogen concentration, which causes the temperature of the microheater to decrease. Pt NP-loaded devices show a similar response when tested in inert environments. This increase in thermal conductivity of the surrounding gas is also evident in the Pt NP-loaded sensor in Figure 7, where at higher  $H_2$  concentrations the response deviates below the expected extrapolation from lower concentrations, as shown by the solid line that is fit to the first four data points in Figure 7.



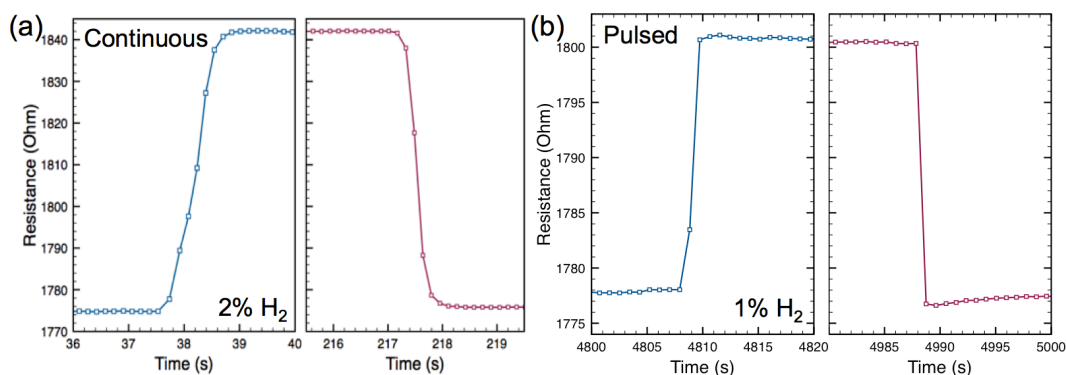
**Figure 7.** (a) Response ( $\Delta R/R_0$ ) of the microheater-based sensor versus hydrogen concentration functionalized with Pt-loaded graphene aerogel and bare graphene aerogel. (b) Response of the sensor in air and in pure nitrogen. Error bars are standard deviation of response during 45 minutes of exposure at selected concentration and if error bars are not seen, they are within the symbol. The microheater is at 11 mW (320 °C).

It is possible that, since the hydrogen gas is balanced in nitrogen, the deviation from linearity observed in Pt NP-loaded graphene aerogel sensor could be explained by impeded catalytic combustion of hydrogen due to a decrease in oxygen concentration. Therefore, the response to 10,000 ppm hydrogen is measured while the oxygen in the gas stream is varied from 10% to 21%. No measureable difference in the sensor response within this oxygen concentration range is observed (Figure 8). Furthermore, implementation of this sensor in a Wheatstone bridge configuration would compensate for the deviation from linearity.



**Figure 8.** Relative sensor response to 10,000 ppm hydrogen at various oxygen concentrations.

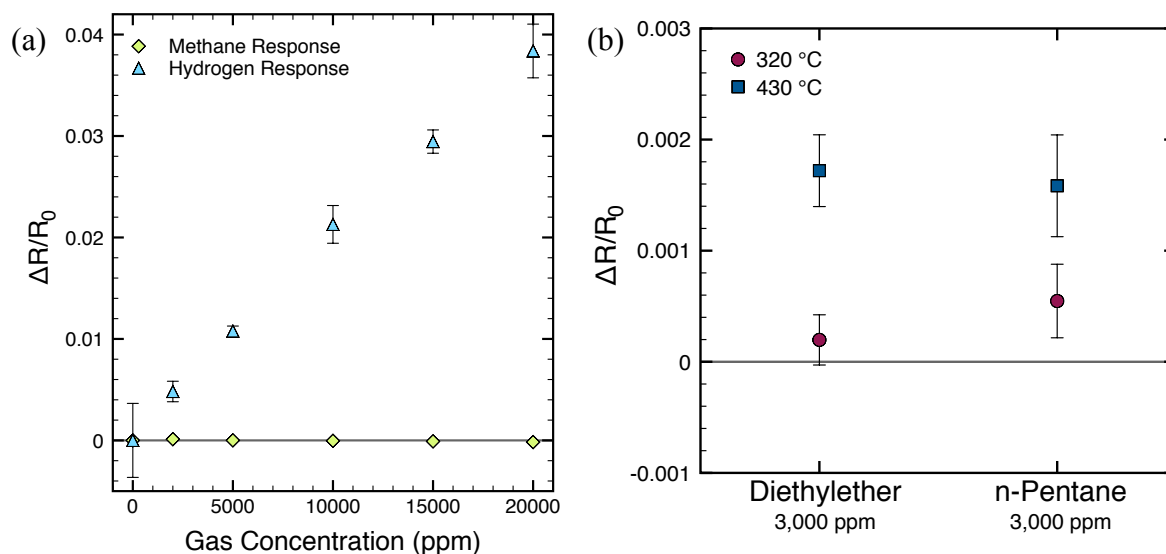
In addition to sensitivity, response time and recovery time are critical metrics for hydrogen sensing. For applications where leak detection is critical for safety, especially hydrogen generation or storage in indoor spaces, a sensor response time of  $\sim 1$  s is required [88]. Figure 9a shows the response and recovery of the sensor operating in continuous heating mode at 11 mW ( $320^\circ\text{C}$ ) for a hydrogen exposure of 20,000 ppm. The  $t_{90}$  response and recovery times are 0.98 s and 0.72 s, respectively. When the sensors are operated in voltage pulsing mode, there is no measureable effect on sensor response or recovery time, as it responds and recovers in one to two data points (1-2 seconds, Figure 9b).



**Figure 9.** (a) Response time and recovery time of sensor when exposed to 20,000 ppm hydrogen. Microheater is powered continuously at 11 mW and data is collected every 150 ms. (b) Response and recovery time of sensor when exposed to 10,000 ppm hydrogen using pulsed heating mode ( $\sim 0.2$  s at 11 mW every 1 s).

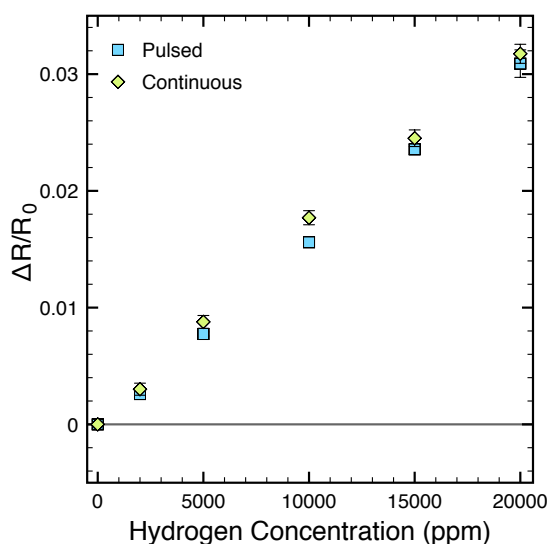
The microheater sensors functionalized with Pt NP-loaded graphene aerogel catalyst are also tested for selectivity. A common interfering gases for hydrogen sensing is methane. Sensitivity to methane is tested for a range of concentrations up to 20,000 ppm. Figure 10a shows the sensor response versus concentration of methane (green, diamonds) and hydrogen (blue, triangles) while heated to 11 mW. There is no measurable response to methane at this power. In fact, detection of methane was not observed even up to 15 mW (430 °C). This indicates that either this catalyst is not capable of catalytically combusting methane or that it requires a higher temperature, in which case an alternative catalyst support with higher thermal stability, such as boron-nitride aerogel [107], would be required.

The selectivity of the catalyst to hydrogen was also tested using two hydrocarbons with low auto-ignition temperatures: diethylether (160 °C) and n-pentane: (260 °C). Figure 10b shows the sensor response to 5,000 ppm of these two gases at 320 °C and 430 °C. At 320 °C, the response is extremely small (equivalent to <100 ppm of hydrogen). At 430 °C, the sensor response is significantly larger, but still only equivalent to approximately 800 ppm hydrogen. The combustion of these hydrocarbons would release more heat per mole than hydrogen, so the small signal obtained shows that Pt nanoparticles cannot effectively catalyze the combustion in this temperature range. In addition, even though the microheater is heated above the auto ignition temperature of both gases, the small thermal mass of the microheater prevents significant auto ignition. Other groups have noted that this feature in microheater-based combustible gas sensors may eliminate the need for bulky, expensive explosion-proof housing, which limit sensor miniaturization and adversely affect sensor response times [108]. The improved selectivity at 320 °C is an added justification for the optimized sensor operating temperature.



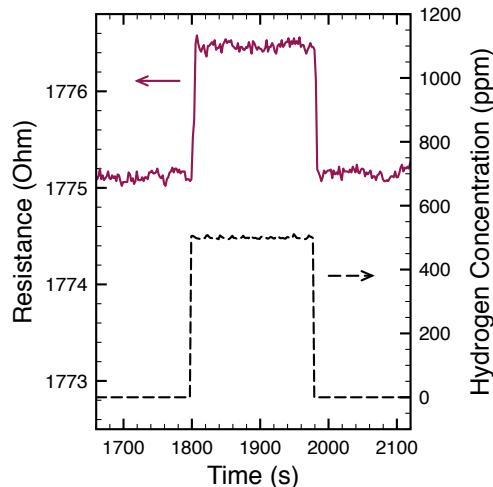
**Figure 10.** (a) Response to methane (green, diamonds) at several concentrations compared to response to hydrogen (blue, triangles). (b) Average sensor response to 3,000 ppm of diethylether and n-pentane at different microheater temperatures. Error bars are the standard deviation of sensor response during 30 minutes of exposure. Microheater is at 11 mW (320 °C).

Using a low duty cycle heat pulse measurement, so the sensor is heated for only part of the time, decreases the power consumption significantly. To ensure that this pulsing of the heater does not affect the sensitivity of the sensor, the response measured when pulsing the heater is compared to the response when continuously heating the sensor. Figure 11 shows the response of the sensor versus hydrogen concentration when heated to 320 °C for 500 ms every 2.5 seconds (blue squares) and when heated continuously at 320 °C. The response difference between pulsed and continuous mode at any concentration is <10%, and the overall linear calibration differs by only 2%. Meanwhile, the power consumption drops 80% from 11 mW to 2.2 mW. For the pulsed heating mode, the sensitivity determined from a linear fit of the data in Figure 9 is 1.6% per 10,000 ppm hydrogen. This corresponds to a sensitivity of 17 mV/10,000 ppm hydrogen if operated in a Wheatstone bridge configuration with a reference sensor with resistance  $R_0$ . This is comparable to many of the commercially available sensors [25], but with much lower power consumption. In addition, over a ten-day testing period with over 60 hours of testing, the sensor displayed good reproducibility with an average change in resistance ( $\Delta R/R_0$ ) of  $0.015 \pm 0.0015$  during exposure to 10,000 ppm hydrogen.



**Figure 11.** Sensor response versus hydrogen concentration for pulsed (pink diamond) and continuous (blue square) modes. Error bars are standard deviation of all data points taken at a given hydrogen concentration during a 3 hour test. Continuous heating is to 11 mW (320 °C) and pulsed heating is 500 ms at 11 mW (320 °C) every 2.5 s.

Finally, the limit of detection of the Pt-NP loaded graphene aerogel-based sensors was determined. Figure 12 shows the sensor response to 500 ppm of hydrogen while operating in pulsed heating mode (500 ms at 320 °C every 2.5 s). The sensor response to 500 ppm of hydrogen is easily distinguishable with a signal to noise ratio of 20-to-1. As mentioned previously, although the sensor is only heated for a fraction of the time, the response time is approximately the same as the continuously heated sensor (within one data point, data collected every 2.5 s). Concentrations lower than 500 ppm were not tested, due to dilution accuracy of the gas delivery system. However, using a signal to noise threshold of 3, the sensor should be able to detect hydrogen down to 65 ppm.



**Figure 12.** Sensor resistance (burgundy line) versus time during a 500 ppm hydrogen exposure (black dashed line). Microheater is pulsed for 500 ms at 11 mW (320 °C) every 2.5 s.

## 5. Conclusion

A low-power catalytic hydrogen gas sensor has been developed using a micro-machined polysilicon heater functionalized with Pt nanoparticle-loaded graphene aerogel as the catalyst material. The graphene aerogel provides a high surface area for platinum nanoparticle loading and high thermal conductivity for efficient transfer of heat generated from the catalytic combustion of hydrogen. The Pt-NP loaded graphene aerogel are characterized using TEM, SEM, and EDAX confirming the homogeneous distribution of small (~6 nm) Pt nanoparticles within the graphene aerogel. The operation temperature of the sensors was optimized for sensitivity, stability, and selectivity. Using a low duty cycle heat pulse measurement, the microheater functionalized with Pt NP-loaded graphene aerogel consumes as low as 2.2 mW of power without compromising the sensor performance. The sensors have a sensitivity of 1.6% per 10,000 ppm hydrogen with a  $t_{90}$  response and recovery time of 0.97 s and 0.72 s, respectively. The sensor shows negligible cross sensitivity to other flammable gases, including methane, n-pentane, and diethylether. A lower detection limit of approximately 65 ppm is estimated.

Further investigations into various catalyst materials to tune selectivity and utilization of catalyst supports with higher thermal stability, such as BN aerogel, should result in detection of other flammable gases, such as methane. Using the low-power microheater platform reported here functionalized with various catalysts and supports, a multi-analyte detection chip can be produced with a very small footprint, thereby enabling wireless battery powered gas detectors at minimal cost for industrial and consumer applications.

## Chapter 4. Nanoparticle-Loaded Graphene Aerogel for Hydrocarbon Sensing<sup>3</sup>

### 1. Motivation

Sensing combustible gases is critical for hydrogen and hydrocarbon leak detection, industrial safety, and environmental monitoring. Combustible gas sensors detect a temperature change caused by surface-catalyzed combustion of the target gas. To promote combustion, the catalyst material must be heated to high temperatures ( $> 450\text{ }^{\circ}\text{C}$ ), which typically requires power consumption of 500 mW or more [1]. This severely limits the ability for these sensors to be battery-powered.

Microfabricated combustible gas sensors have been developed to lower the power consumption required for heating [9]. Our designed platform uses a doped polysilicon microheater. Because polysilicon has higher resistivity than platinum, the heated area can be minimized without electro-migration issues. Shrinking the size allows for our microheater platform to reach  $450\text{ }^{\circ}\text{C}$  with only 14 mW. Additionally, the fast thermal response time of the heater allows for rapid duty cycling that lower the power consumption even further.

Progress in microheater development has revealed the need for novel catalytic materials tailored for the microfabricated sensors. Typical catalyst materials have been the same noble metal nanoparticles on porous oxides used in commercial devices. These have poor thermal conductivity and gas diffusion leading to slow response (10-20 s) [9], [15], [108], as well as issues with integration and adhesion on the microheaters.<sup>[4]</sup> Some researchers have looked to thin films, which can be better integrated into sensor manufacture, but the lower surface area leads to poor sensitivity [15], [109]. Use of graphene aerogel (GA) with high surface area and high thermal conductivity as a support for catalytic nanoparticles is an attractive approach that maintains high surface area of catalyst for good sensitivity, and improves response and recovery time [102], [110]. Chapter 3 describes the use of platinum nanoparticles on graphene aerogel for hydrogen sensing with fast response and recovery ( $<1\text{ s}$ ), which is attributed to minimized support mass and improved thermal conductivity of the support [110].

Here platinum and palladium nanoparticles on high surface area GA (approx.  $900\text{ m}^2\text{ g}^{-1}$ ) are investigated as catalytic materials for both hydrogen and propane sensing. The GA used here has a higher pyrolysis temperature of  $2000\text{ }^{\circ}\text{C}$ , which gives it improved crystallinity and thermal stability over the GA pyrolyzed at  $1050\text{ }^{\circ}\text{C}$  used in Chapter 3 [100]. Expanding the types of nanoparticles loaded on the graphene aerogel demonstrates the versatility of this approach and opens the possibility of selective sensing with an array of materials. Response and recovery times are within 1-2 seconds for the various metal-gas combinations. The fast response time of both the microheater and the catalyst material open up the possibility of fast temperature

---

<sup>3</sup> A modified version of this work was published in A. Harley-Trochimczyk, J. Chang, T. Pham, J. Dong, M.A. Worsley, A. Zettl, W. Mickelson, R. Maboudian. "Low power microheater-based combustible gas sensor with graphene aerogel catalyst support," Proceedings of the 18<sup>th</sup> Int'l Conference on Solid-State Sensors and Actuators, Transducers '15, pp. 1483-1486 (2015).

scanning to build in selectivity or duty cycling to decrease power consumption even further. No loss of sensitivity is seen for the propane response of platinum nanoparticle-loaded graphene aerogel with 10% duty cycling, which corresponds to power consumption of only 1.4 mW. Sensor response stability remains a challenge, but using the graphene aerogel catalyst support signals the potential for truly low power combustible gas sensing.

## 2. Material synthesis and characterization

### 2.a. Graphene aerogel

Graphene aerogel synthesis is described in detail in Chapter 3. Briefly, graphene oxide sheets are added to water and ammonium hydroxide and heated at 85 °C to promote gelation. The scaffold is dried through critical point drying to retain the pores and pyrolyzed under nitrogen at 1050 °C to reduce the oxygen-containing groups. Here, an additional pyrolysis step is performed for 1 hour in helium to improve the quality of the final aerogel. Worsley, et al., report the resulting aerogel characteristics for a secondary anneal at 1500, 2000, and 2500 °C [100]. The specific surface area decreases with higher anneal temperatures, but the thermal stability improves as the aerogel becomes more crystalline and graphitic. At 1500 °C, the specific surface area remains 1200 m<sup>2</sup> g<sup>-1</sup>, while at 2000 °C, it is 900 m<sup>2</sup> g<sup>-1</sup> and falls to 345 m<sup>2</sup> g<sup>-1</sup> at 2500 °C. The change in surface area is attributed to an increase in crystallinity and subsequent loss of pores in the 2-10 nm size range and increase in multi-layer regions in the aerogel.

Thermogravimetric analysis of the aerogels annealed at different temperatures shows the improvement in thermal stability for those pyrolyzed at higher temperature, with 50% mass loss going from 560 °C for the GA pyrolyzed at 1050 °C to 770 °C for the GA with a secondary anneal at 2500 °C [100]. Taking both the specific surface area and thermal stability into account, the 2000 °C-annealed graphene aerogel is selected for use as the scaffold material for catalytic nanoparticles.

The specific surface area of 900 m<sup>2</sup> g<sup>-1</sup> for the graphene aerogel is much higher than typical values for porous alumina (~100 m<sup>2</sup> g<sup>-1</sup>), the most common catalyst support material used in combustible gas sensing [111]. The in-plane thermal conductivity of the graphene aerogel, which is composed of cross-linked few layer graphene sheets, is also several orders of magnitude higher than that of alumina (~1000 W m<sup>-1</sup> K<sup>-1</sup> for few layer graphene [112] vs. ~10 W m<sup>-1</sup> K<sup>-1</sup> for alumina [113]).

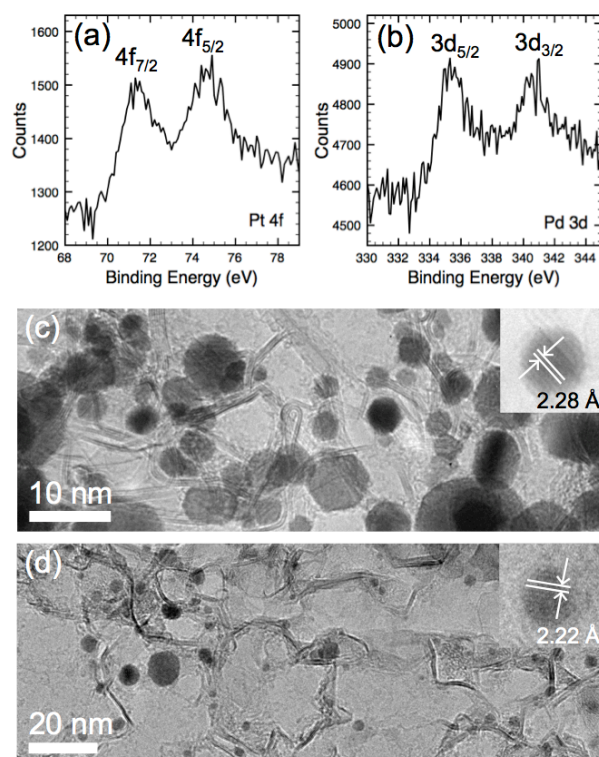
### 2.b. Platinum and palladium-nanoparticle loading

Platinum nanoparticle loading follows the process detailed in Chapter 2, where the aerogel is soaked in a 0.5 M aqueous solution of chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>), freeze-dried, and thermally reduced under hydrogen flow at 450 °C to form pure metallic nanoparticles. Palladium nanoparticle loading is similar, but with palladium chloride (PdCl<sub>2</sub>) as the precursor and a solution concentration of 0.1 M.

Successful loading of Pt and Pd nanoparticles is confirmed with X-ray photoelectron spectroscopy (Figures 1a and 1b) as well as transmission electron microscopy (Figure 1c and 1d). For the Pt nanoparticles, about 70% have a 1-2 nm radius, with the rest up to 10 nm radius. For the Pd nanoparticles the distribution is tighter, with about 70% at a 1-2 nm radius and the rest larger, up to 5 nm. The density of Pd nanoparticles is lower because a lower concentration of the



metal salt was used. The Pt lattice spacing of 2.28 Å is consistent with the Pt(111) crystal plane, and the Pd lattice spacing of 2.22 Å is consistent with the Pd(111) crystal plane (insets of Figure 1c and 1d respectively).

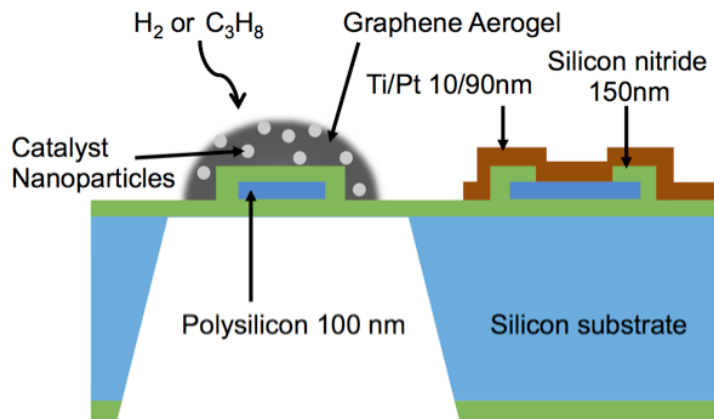


**Figure 1.** (a) XPS spectra of Pt 4f and (b) Pd 3d spectral regions confirm nanoparticle loading on GA. (c) TEM of Pt-GA. (d) TEM of Pd-GA. Insets show lattice spacing.

### 3. Sensor fabrication and testing

The polysilicon microheater platform described in Chapter 2 is used here. Nanoparticle-loaded graphene aerogel is suspended in water and drop-cast onto the microheater to form the sensor. Figure 2 is a schematic showing the catalytic material integrated on the microheater platform. Fabricated sensors are wirebonded into a CerDIP package and placed in a 1 cm<sup>3</sup> gas chamber, as described in Chapter 3. Gas flow is controlled with mass flow controllers (Bronkhurst) and Labview. Sensor measurements are performed with a Keithley 2602 sourcemeter. Hydrogen and propane gas tanks are 5% (50,000 ppm) balanced in nitrogen (Praxair). Hydrogen gas is diluted with dry, clean air to reach the concentrations tested, while propane gas is mixed with nitrogen and oxygen to maintain an oxygen concentration of 20%. Chapter 3 shows no hydrogen response dependence on the percentage of oxygen in the range of 10-21%, so it is not critical to maintain an exact oxygen concentration. The reason the oxygen concentration changes with house air used for stream balance is that a total flow rate of 300 sccm is used with various hydrogen concentrations. Since the combustible gas tanks are balanced in nitrogen, at high concentrations of hydrogen where the flow rate of air required for a total rate of 300 sccm is smaller, there is less oxygen. As an example, for a hydrogen concentration of 2%, a flow rate of 120 sccm comes from the hydrogen tank with the rest from house air. This gives an oxygen concentration of

12.6% (21% of 180 sccm air in a total of 300 sccm). As will be shown in Chapter 5, there is a large change in propane response at varied oxygen concentration, so a constant oxygen concentration is used to eliminate this factor.



**Figure 2.** Sensor schematic.  $\text{H}_2$  or propane gas reacts on the catalyst nanoparticle surface and releases heat, causing increased temperature of the polysilicon, resulting in a resistance increase.

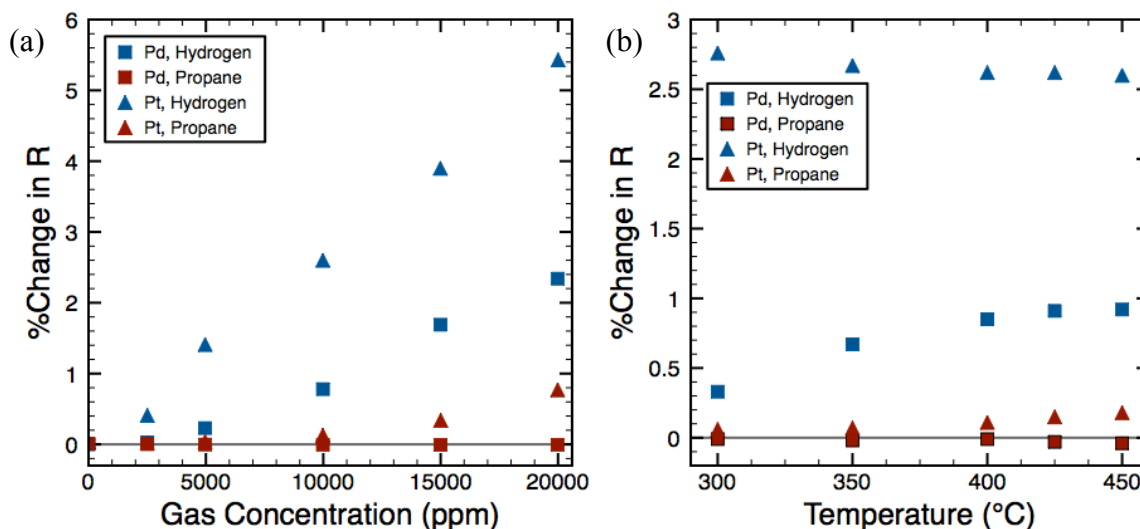
## 4. Sensing Results

### 4.a. Sensitivity and response time

Building upon prior work on hydrogen gas sensing, the practicality of the sensor for general combustible gases is tested using propane gas. Propane is a colorless, odorless gas that is produced as a byproduct of natural gas processing and petroleum refining. It is commonly used for heating, cooking, and power generation, especially in areas without access to natural gas pipelines [114]. Propane is also used to enhance oil recovery in oil wells and as a raw material in the petrochemical industry [114], [115]. Recently, propane has also been explored as an environmentally-friendly alternative to traditional chlorofluorocarbon refrigerants at both the residential and industrial scale [116], [117]. However, propane, like other hydrocarbons, poses certain safety hazards. It is explosive in air, with a lower explosive limit of 2.1% (21,000 ppm) in air and an autoignition temperature of 450 °C [118]. Since propane is routinely used in environments containing ignition hazards, both at the residential scale (stovetop burners, pilot lights, etc.) and at the industrial scale (gas flares, welding, electric power systems, etc.) [118], it is important to install systems capable of monitoring propane levels and detecting leaks before they can become explosive hazards.

The sensitivity of the nanoparticle-loaded graphene aerogel sensor is defined as  $R - R_0 / R_0 \times 100\%$  (%Change in R) where R is the average resistance during a given exposure and  $R_0$  is the average resistance with 0 ppm concentration. Figure 3a shows the result of hydrogen and propane exposure to the Pt nanoparticle-loaded GA sensor (Pt-GA) and Pd nanoparticle-loaded GA sensor (Pd-GA) at the optimum response temperature for each metal-gas combination. For Pt-GA the optimum temperature for hydrogen response is 300 °C, as seen in Figure 3b. For Pd-GA, hydrogen sensitivity plateaus at 400 °C. The peak in response corresponds to a shift from a kinetic-controlled regime to a mass transfer-limited regime. Further increases in temperature in this regime may decrease sensitivity by making gas adsorption less favorable. Even if the

response does not decrease, the more limited gains in sensitivity are not worth the additional power consumption required to operate at the higher temperature. For propane, there is no response for Pt-GA below 350 °C, but the GA has limited stability at high temperature, thus 450 °C is chosen as the optimal temperature for propane response to balance sensitivity and thermal stability. Pd-GA shows no response to propane even up to 450 °C (Figure 3a).

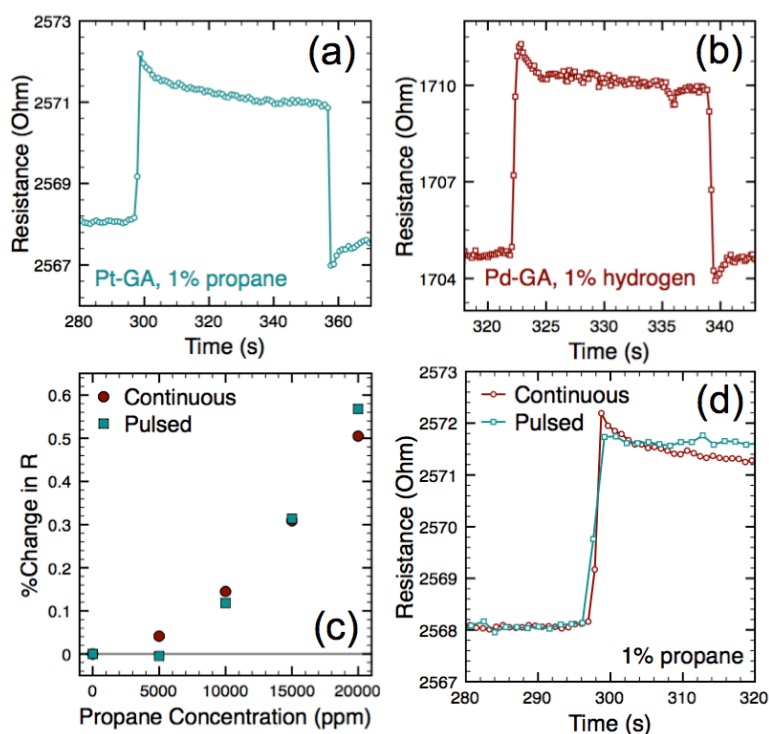


**Figure 3.** (a) Average response,  $(R-R_0)/R_0 \times 100\%$ , for Pt-GA and Pd-GA plotted versus gas concentration at optimum temperatures for each metal-gas combination. (b) Response of each metal-gas combination to 1% gas at various temperatures.

There is a noticeable difference in the limit of detection between hydrogen and propane for the Pt-GA sensor. Even though propane combustion releases more heat per mole, the sensitivity is lower because of the different activity levels of propane and hydrogen combustion on platinum. Because the limit of detection is controlled by the level of background noise and the temperature coefficient of resistance (TCR) of the microheater, using a microheater material with higher stability of the resistance and a larger TCR may improve the sensitivity and the limit of detection. However, it is also important to note that the limit of 5,000 ppm for propane may be an artifact of the gas delivery system. There are two mass flow controllers for each gas tank, one for high flow rates (up to 1200 sccm) and one for low flow rates (up to 25 sccm). For a total flow rate of 300 sccm, which is what is used in these experiments, and given a tank concentration of 5%, the switch from the high MFC to low MFC happens between 4,000 and 5,000 ppm propane or hydrogen. The low MFC seems to have a slightly different calibration, which leads it to deliver a lower concentration than expected. In Figure 3a, for the Pt-GA response to hydrogen, the response to 2,500 ppm is clearly lower than expected from the linear response curve of the higher concentrations. Another factor is that the propane response at 450 °C has not yet reached a mass transfer limited regime. So when the combustion starts, it raises the sensor temperature, which increases the rate, which increases the temperature and so on, in a positive feedback loop. The implication is that there may be a critical concentration where the feedback loop takes over and results in a visible response.

The observed differences in response between Pt-GA and Pd-GA may arise from differences in catalyst loading and inherent different in interaction between each metal and the gas. With this microheater platform, the maximum power consumption is 14 mW (to reach 450 °C). Given the sensor response towards different gases varies with both temperature and catalyst material (Pt vs. Pd), a selective combustible gas sensor array can be constructed.

Prior work for hydrocarbon sensing on porous alumina catalyst supports shows response times on the order of 20 s [17], [108]. Response and recovery times for Pt-GA exposure to propane and Pd-GA exposure to hydrogen are shown in Figure 4a and 4b and are seen to be fast in both cases (within 1-2 s). The high thermal conductivity of the graphene aerogel may allow for faster transfer of combustion heat to the sensor. Also, the high specific surface area means less support material is used for the same platinum loading, minimizing the power needed for heating the support.

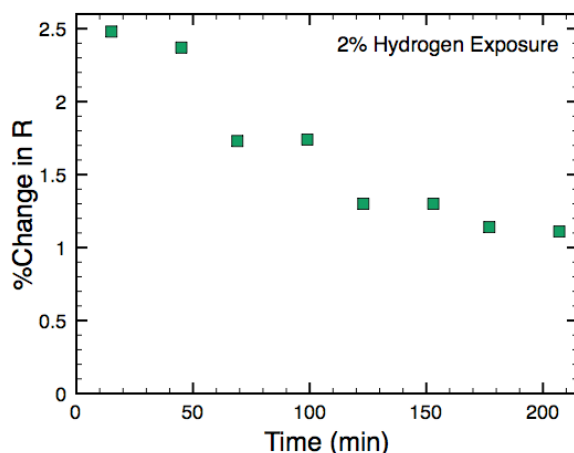


**Figure 4.** Response and recovery to (a) 1% propane for Pt-GA and (b) 1% hydrogen for Pd-GA. (c) Sensitivity of Pt-GA to propane for continuous heating and pulsed heating. (d) Response time for Pt-GA to 1% propane for continuous heating and pulsed heating.

The fast response and recovery also enable duty cycling with no loss of sensitivity. For example, the Pt-GA sensor was tested for propane response with continuous heating at 450 °C and with a 10% duty cycle (heating to 450 °C for 100 ms every second, with the sensor at room temperature in between). Figure 4c shows comparable sensitivity between the continuous heating and pulsed heating case and Figure 4d shows the response time during pulsed heating is slightly longer, but still within a few seconds. With this strategy, power requirements are in the single mW range.

#### 4.b Response stability

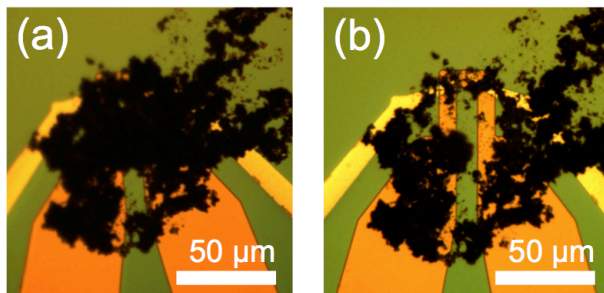
In addition to good sensitivity and fast response and recovery, the sensor response stability is critical for practical application. Studies of the response stability of the palladium nanoparticle-loaded graphene aerogel show a substantial drop in hydrogen response over a few hours (Figure 5). Palladium is known to form a palladium hydride phase upon exposure to hydrogen [119], [120]. This fact is actually exploited in a number of hydrogen sensing mechanisms [121]–[123], where the hydride formation changes the material conductance through a work function change or even a volumetric change. However, in this case where the palladium nanoparticles are meant to act as a catalyst for hydrogen combustion, the hydride phase formation seems to negatively impact the catalytic activity and thus, the sensor response. If the hydride phase formation is not fully reversible, a gradual accumulation of the hydride phase will occur with repeated hydrogen exposure.



**Figure 5.** Pd-GA response to 2% hydrogen decreasing over the first few hours of testing.

This has important considerations for combustible gas sensor design because palladium is often used as a catalytic material either alone or in combination with platinum because of its high activity for hydrocarbon combustion [7]. If the combustible gas mixture is expected to contain hydrogen, a palladium-containing sensor may be adversely affected.

Even with the additional pyrolysis step to improve the thermal stability, the graphene aerogel has issues with stability during the high operating temperatures required for propane combustion. In addition to high baseline temperature, propane combustion during sensing can significantly raise the temperature of the sensing material. When the Pt-GA was exposed to 2% propane with the microheater initially at 450 °C, the temperature is estimated to increase to 725 °C, which is above the stability point of the graphene aerogel, which loses 50% of its mass when heated in air to 700 °C [100]. The resistance increase during the initial exposure to 2% propane is 0.9% above the baseline value of 2568  $\Omega$ . Using the resistance versus temperature calibration relationship (see Chapter 2), the new resistance (2590  $\Omega$ ) can be correlated to a temperature of 725 °C. This leads to a visible loss of material (Figure 6), although the sensing response does not completely disappear.



**Figure 6.** Optical images of Pt-GA on the microheater (a) before testing; (b) after several hours of propane testing with microheater at 450 °C.

## 5. Conclusions

A combination of a low power microheater and improved catalyst support opens possibilities for low power and selective combustible gas sensing. The high specific surface area graphene aerogel allows for high loading of catalyst nanoparticles while improving the response and recovery time for both hydrogen and propane gas to 1-2 s. A high temperature anneal during the graphene aerogel synthesis improves the thermal stability, although not enough for sustained operation at high temperature. The graphene aerogel can be loaded with various catalytic nanoparticles, which give different sensitivity and selectivity for hydrocarbon detection.

Palladium nanoparticle-loaded graphene aerogel responds selectively to hydrogen over propane, while platinum nanoparticle-loaded graphene aerogel responds to both hydrogen and propane, although the response to hydrogen is higher. Using these different materials, a selective sensor array can be assembled. The fast response of the microheater and the catalyst support means pulsed heating can be used to lower the power consumption to the single mW range without losing sensitivity (only 1.4 mW for 10% duty cycling of Pt-GA for propane response).

Selectivity can also be enabled by rapidly scanning temperatures or pulsing various elements in the array, to keep the power consumption low. Instability with the graphene aerogel at high temperature points out the limitations of this class of nanomaterials and the need for other support materials, such as boron nitride, that retain the advantages of high surface area and thermal conductivity, while possessing improved thermal stability.



## Chapter 5. Platinum Nanoparticle-Loaded Boron Nitride Aerogel for Catalytic Gas Sensing<sup>4</sup>

### 1. Motivation

Hexagonal boron nitride (h-BN) is a 2D material that has generated great interest due to its unique optical, electrical, and thermal properties [124]–[126]. It is the most stable form of crystalline BN. While structurally similar to graphite and graphene, h-BN has a distinct set of complementary and, in many cases, advantageous properties compared to its carbon analogs. For example, h-BN is a wide band gap insulator (independent of morphology), yet has high thermal conductivity, high resistance to oxidation, and the lowest density among non-oxide ceramics [127]–[129]. Having a similar  $sp^2$ -bonding configuration to graphite, h-BN can be synthesized in analogous lower dimensional forms such as nanotubes (1D) [130], [131] and nanosheets (2D) [132], [133], which have high specific surface area, among their other qualities. To exploit the high surface area of these nanomaterials in a 3D geometry, there have been efforts to synthesize low density 3D structures of BN comprised of lower dimensional nanomaterials [107], [134]–[136]. These high surface area 3D BN materials have been proposed for hydrogen storage [137]–[140], hydrocarbon uptake [141]–[143], and water purification [139], [144] due to the enhanced physisorption properties of BN compared to carbon [145]. In addition to these applications, high surface area BN is an interesting candidate as a support material for optically or catalytically active nanoparticles, due to its wide band gap and chemical inertness. Nanoparticle loaded-boron nitride has been studied for use in high temperature or harsh environment catalysis applications in gas [146]–[149] and liquid phases [150]. In these previous catalysis-focused works, the porous BN is of varying crystallinity and specific surface area, and many of the synthesis processes for the porous BN and the nanoparticle decoration rely on hazardous liquid precursors and reducing species. Recently, a novel method for the synthesis of highly crystalline, high specific surface area,  $sp^2$ -bonded boron nitride aerogels using non-hazardous reactants has been developed [107]. In this work, loading of this highly crystalline, high surface area, mesoporous boron nitride aerogel with well-dispersed platinum nanoparticles is reported and as an example of its utility, low power, fast, and sensitive catalytic gas sensing is demonstrated.

To assess the catalytic activity and stability of the Pt nanoparticle-loaded boron nitride aerogel (Pt-BN) presented here, the aerogel is integrated onto a microheater to form a catalytic gas sensor or micropellistor. Low power catalytic gas sensors are in demand for fast leak detection in hydrogen and hydrocarbon generation, handling, storage, and transport. Early warning of leaks will result in increased safety and environmental protection. Research efforts have focused on porous alumina supports [15], [24], [30], which suffers from low thermal conductivity, and thin films of catalytic metals [15], [28], [109], [151], which have low active surface area. Boron nitride aerogel offers enhanced thermal conductivity compared to alumina, and a high surface area for increased nanoparticle loading in a constrained volume of the microfabricated sensor.

---

<sup>4</sup> A modified version of this work was published in A. Harley-Trochimczyk, T. Pham, J. Chang, E. Chen, M. A. Worsley, A. Zettl, W. Mickelson, R. Maboudian. “Platinum nanoparticle loading of boron nitride aerogel and its use as a novel material for low-power catalytic gas sensing,” *Advanced Functional Materials*, vol. 26, pp. 433-439, 2016.

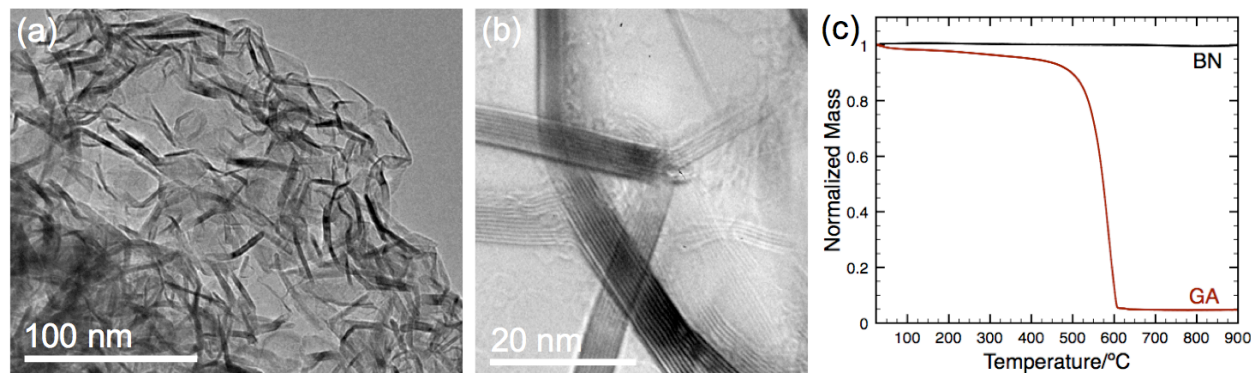
Increased thermal conductivity of the support allows heat generated during gas combustion to be efficiently transferred to the microheater and raise its temperature. Catalytic gas sensing using the newly developed Pt-BN demonstrates the advantage of this material.

## 2. Material synthesis and characterization

Boron nitride aerogel acts as an ideal catalyst support due to its high specific surface area, good thermal stability, and high thermal conductivity. BN aerogel synthesis follows the procedure of Ref. 107 where graphene aerogel (GA) is converted to boron nitride aerogel through the carbothermic reduction of boron oxide and concurrent nitridation with nitrogen gas at high temperature (1600-1800 °C) [107]. The resulting few layer  $sp^2$ -bonded BN maintains the microporous structure of the graphene aerogel and has a high specific surface area ( $\sim 500 \text{ m}^2 \text{ g}^{-1}$ ). The high specific surface area allows, in principle, for high catalyst nanoparticle loading while minimizing the mass of the catalyst support. Furthermore, BN exhibits a high resistance to oxidation at elevated temperature [124], which is paramount to robust long-term operation in high temperature catalysis applications. The synthesized BN aerogel also maintains a high degree of crystallinity imparted by the graphene aerogel, and in fact, the degree of crystallinity may increase during the conversion process [107]. The highly crystalline aerogel allows the thermal conductivity of the h-BN to be preserved better than a porous BN structure with less order. Hexagonal BN has high in-plane thermal conductivity ( $\sim 250 \text{ W m}^{-1} \text{ K}^{-1}$  [128]), especially compared to alumina, the most common catalyst support ( $\sim 10 \text{ W m}^{-1} \text{ K}^{-1}$  [113]). The thermal conductivity of the BN aerogel allows heat generated during exothermic reactions to be more effectively dissipated. Without this heat dissipation, hot spots can build up and cause sintering of the catalytic nanoparticles or damage to the support itself.

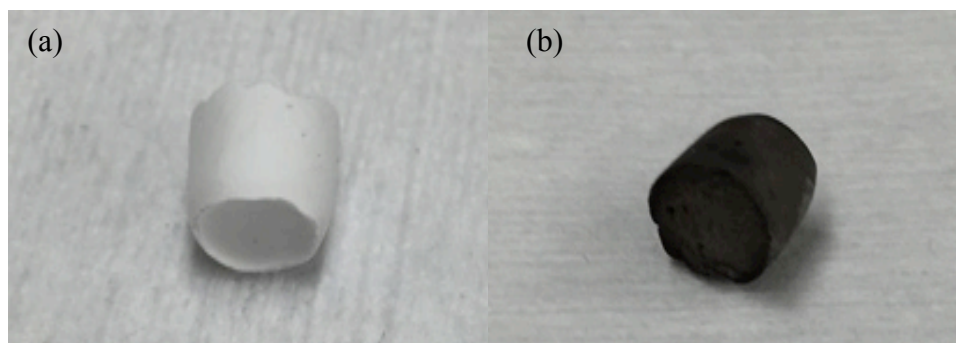
The as-synthesized BN aerogel can be seen in Figure 1a with a transmission electron microscopy (TEM) image showing the wrinkled BN sheets displaying features on the tens of nanometers scale. As seen in the high-resolution TEM image in Figure 1b, the aerogel is comprised of highly crystalline few-layer BN. The junctions between BN sheets within the aerogel are comprised of covalent bonds, which lead to improved thermal conductivity compared to randomly stacked BN sheets [152]. Thermogravimetric analysis (TGA) of the BN aerogel compared to the GA starting material shows the improved thermal stability, with GA showing a 50% loss in mass by 575 °C, while the BN aerogel has <1% change in mass during heating up to 900 °C (Figure 1c).





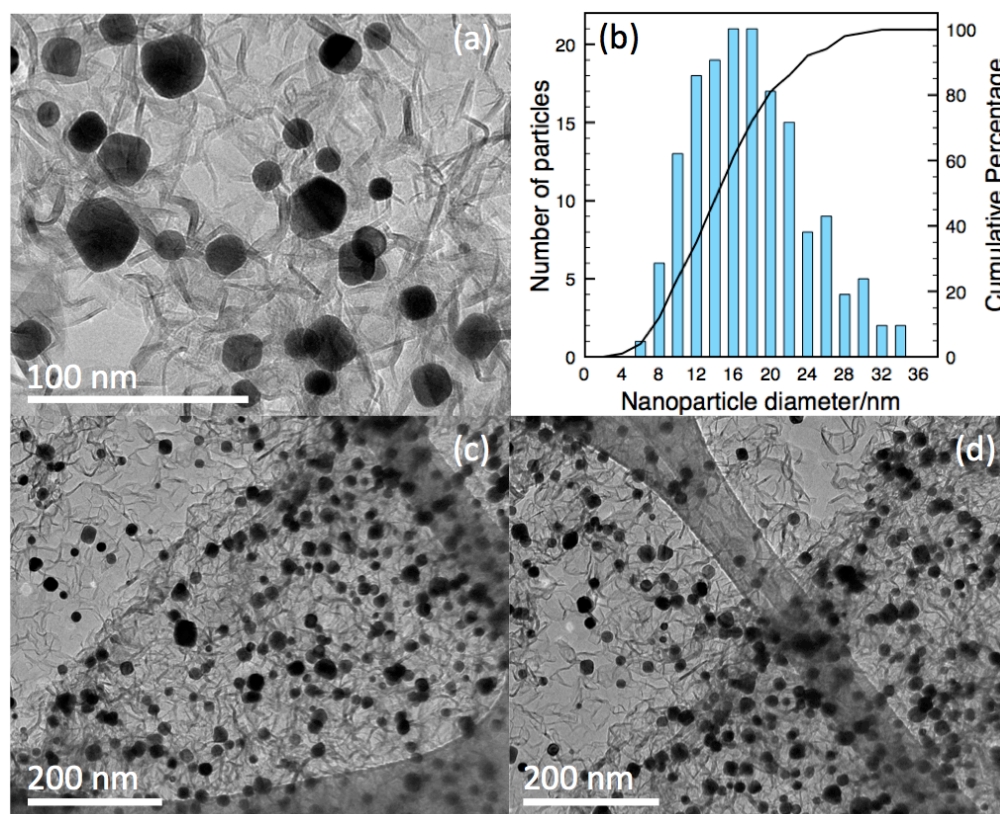
**Figure 1.** (a) TEM of bare boron nitride aerogel. (b) High resolution TEM of boron nitride aerogel showing highly crystalline, few layer BN. (c) Thermogravimetric analysis (TGA) of boron nitride aerogel (BN) [143] and graphene aerogel (GA) [100], showing improved thermal stability of the BN aerogel. TGA is done in 20% O<sub>2</sub>/Ar with a ramp rate of 10 °C min<sup>-1</sup>.

Noble metals, especially platinum and palladium, have been widely used for catalysis, especially oxidation reactions that require high temperatures for appreciable reaction rates [8]. Platinum nanoparticle size, crystallinity, and interaction with the support all affect catalytic activity. In this paper, platinum catalyst loading of the BN aerogel is achieved by immersing the aerogel in chloroplatinic acid in ethanol (0.5 M), drying, and annealing in argon (50 sccm) at 600 °C for 2 hours in order to thermally reduce the platinum complex to pure crystalline platinum nanoparticles. Optical images of the BN aerogel before and after platinum loading can be found in Figure 2. From measurement of the aerogel weight before and after platinum loading, a platinum weight ratio of 45% is calculated. Specific surface area of the platinum nanoparticle-loaded boron nitride aerogel is 275 m<sup>2</sup> g<sup>-1</sup>, as calculated from the nitrogen adsorption isotherm using the Brunauer-Teller-Emmett method with a Micromeritics ASAP 2420 porosimeter [104]. The decrease in the specific surface area from the bare aerogel is expected since the high loading of platinum increases the weight without significantly changing the surface area.



**Figure 2.** Optical images of the boron nitride aerogel (a) before and (b) after platinum nanoparticle loading. The monolithic aerogel is synthesized in a test tube which gives it a cylindrical shape roughly 6 mm tall and 6 mm in diameter. The large band gap of boron nitride results in a white appearance. The high loading of platinum nanoparticles results in more light absorption and a black color.

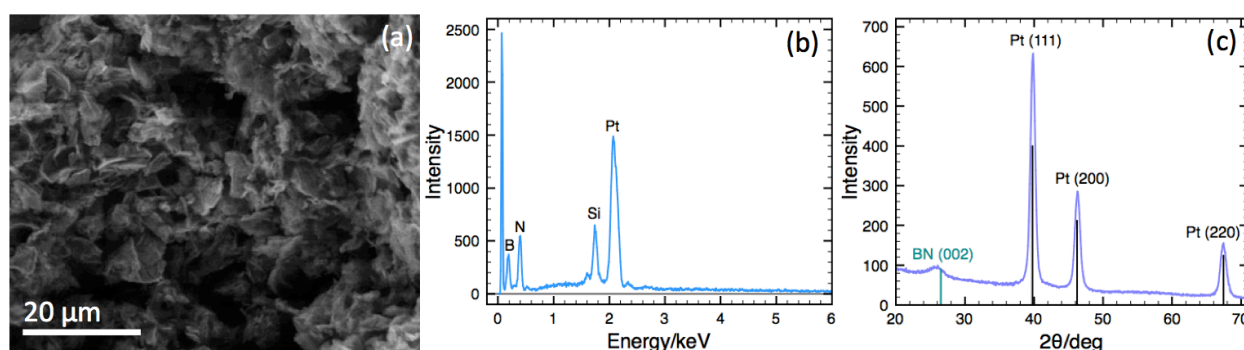
BN and Pt-BN aerogels were dispersed in isopropanol by sonication and then dropped onto a lacey carbon grid for TEM characterization using a JOEL 2010 microscope. In Figure 3a, a TEM image of the platinum nanoparticle-loaded boron nitride aerogel (Pt-BN) confirms the presence of crystalline nanoparticles with average diameter of 17 nm  $\pm$  6 nm, based on 150 particles (distribution of particle size shown in Figure 3b). Additional TEM images used for particle analysis are shown in Figure 3c and 3d.



**Figure 3.** (a) TEM of BN aerogel after Pt nanoparticle loading. (b) Size distribution of platinum nanoparticles. (c) and (d) Additional (larger area) TEM images used for nanoparticle size determination.

Scanning electron microscopy (SEM, FEI Sirion XL30) images of the Pt-BN show that the porosity and high surface area of the aerogel, as seen by TEM, are representative of the entire aerogel structure and are not diminished after the nanoparticle loading process (Figure 4a). To determine the chemical composition and physical structure of the nanoparticles, energy dispersive X-ray spectroscopy (EDAX) and X-ray diffraction (XRD) are performed. The EDAX spectrum in Figure 4b confirms the presence of Pt, as well as B and N (the Si peak is from the sample substrate) with no detectable amount of chlorine, suggesting that the platinum salt has been completely reduced to elemental platinum. No carbon is detected in the EDAX measurements, suggesting complete conversion of the graphene aerogel in the formation of the BN aerogel. The presence of metallic platinum is further confirmed via XRD in Figure 4c, which

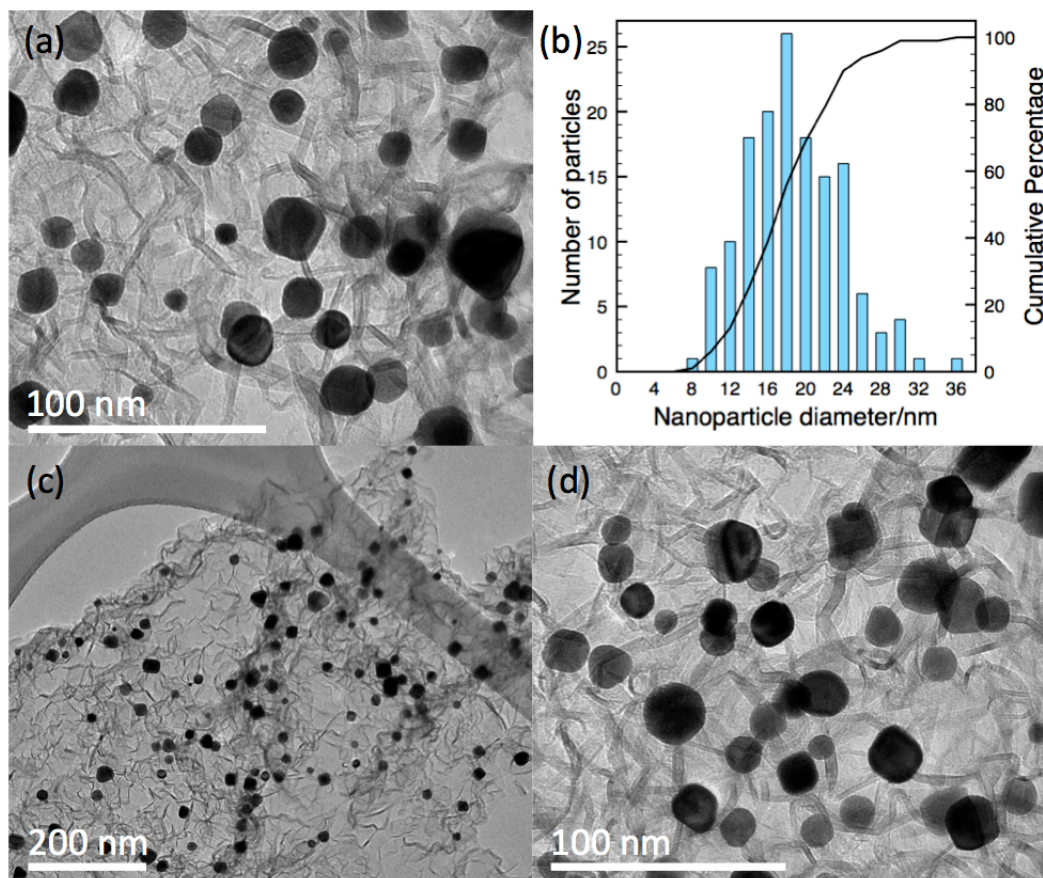
shows the characteristic (111), (200), and (220) peaks of the Pt face-centered cubic structure, as well as the BN (002) peak. X-ray diffraction for elemental and structure analysis used an AXS D8 Discover GADDS diffractometer from Bruker with radiation from a Cu target ( $K\alpha$ ,  $\lambda = 0.154$  nm). The crystalline nature of the platinum nanoparticles is also evident in the faceted shapes observed in the TEM images, as well as the sharp peaks attributed to platinum in the XRD pattern, as seen in Figure 4c. Using the Scherrer formula for the full width at half maximum of the Pt (111) peak with a crystalline shape factor ( $K$ ) of 0.94 for spherical crystals with cubic unit cells, the predicted crystallite size is 9.6 nm, which has good agreement with the particle size analysis from the TEM images [153]. The relatively low intensity of the BN (002) peak in the XRD spectra results from the high loading of platinum and the low density of the BN aerogel.



**Figure 4.** (a) SEM of BN aerogel after Pt nanoparticle loading showing retained porosity and high surface area. (b) EDAX results confirming presence of B, N and Pt. (c) XRD spectra showing BN (002) peak and Pt (111), (200), and (220) peaks.

Interaction between the Pt nanoparticles and the BN support is important for maintaining nanoparticle dispersion, especially during high temperature operation. The Pt-BN reported here maintains good stability of the nanoparticle size and dispersion after heating in air at 500 °C for 24 hours, as shown in Figure 5. No measurable platinum nanoparticle sintering is observed. Analysis of platinum nanoparticle size and size distribution leads to an average particle size of 17.6 nm  $\pm$  5 nm, which is not statistically different from the Pt-BN before heating (Figure 5b). Additional TEM images for size determination are shown in Figures 5c and 5d for a total of 150 nanoparticles analyzed. Prior work has suggested that a high degree of BN crystallinity led to platinum aggregation at elevated temperature due to the weaker interaction of the crystal faces of h-BN with Pt compared to the edges or defects [154]. Despite having a high degree of crystallinity in the boron nitride aerogel reported here, the platinum remains well dispersed and tightly adhered. For the TEM analysis, the Pt-BN is sonicated in IPA for thirty minutes before dispensing on a lacey carbon grid. Despite this, the TEM images show high nanoparticle density on the BN sheets and no free Pt nanoparticles visible on the lacey carbon, indicating a strong interaction between the Pt nanoparticles and BN. Partial encapsulation of the nanoparticle within the pores of the BN aerogel or chemical stabilization from defects at the cross-linking sites within the aerogel may explain the improved platinum dispersion within the BN aerogel. The meso-porosity of the BN aerogel effectively prevents sintering of the platinum nanoparticles, allowing activity to be maintained even during high temperature operation.

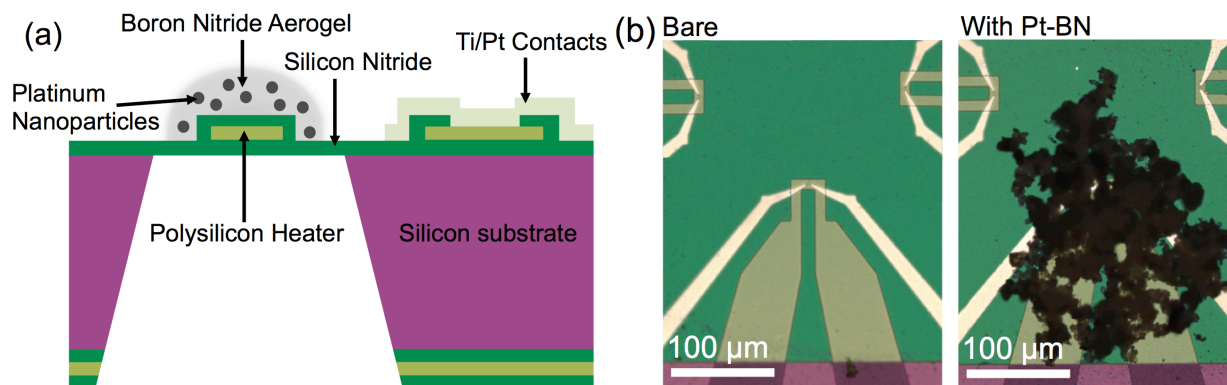




**Figure 5.** (a) TEM image of Pt-BN after heating in open-air furnace for 24 hours at 500 °C shows no sintering or aggregation of platinum nanoparticles. (b) Platinum nanoparticle size distribution. (c) and (d) Additional TEM images of Pt-BN used for nanoparticle size analysis.

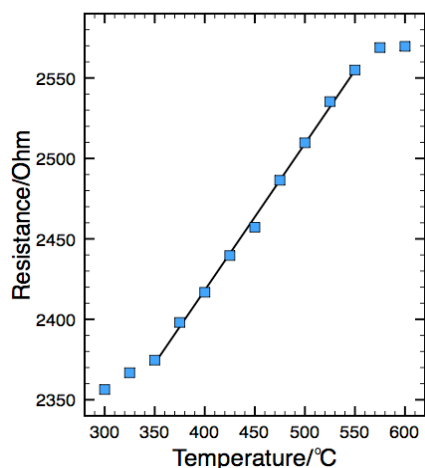
### 3. Sensor fabrication and testing methods

Catalytic gas sensors are prepared by drop-casting a suspension of Pt-BN (or BN) aerogel material onto a low-power microfabricated heater platform. BN and Pt-BN aerogels are dispersed in isopropanol by sonication and drop-cast (6 drops of 0.6  $\mu\text{L}$  each) onto the microheater chip while one of the microheaters is powered to 65 °C to promote solvent evaporation and material deposition at the center of the microheater. The microheater used in this work consists of a polycrystalline silicon (polysilicon) trace encapsulated in a thin silicon nitride membrane, and can reach 500 °C with only 15 mW peak power. Details of the microheater fabrication and characterization have been discussed in Chapter 2. The cross-sectional schematic of the fabricated sensor in Figure 6a and the optical images in Figure 6b show the Pt-BN deposited on the heated area of one microheater.



**Figure 6.** (a) Schematic of sensor cross-section. Pt-BN is drop-cast on top of microheater platform. When sensor is exposed to catalytic gas, the gas reacts with oxygen on the surface of the platinum nanoparticles and releases heat, which increases the temperature and, correspondingly, the resistance of the polysilicon microheater. (b) Optical images of one microheater before and after Pt-BN deposition.

The sensor is placed in a gas flow chamber (1 cm<sup>3</sup> volume). Gas exposure and signal collection are done using Labview and an open-source Java-based instrument and control and measurement software suite, Zephyr. Gas tanks of pure nitrogen, pure oxygen, and 5% propane balanced in nitrogen (Praxair) are controlled with mass flow controllers (Bronkhorst) and mixed to give the desired oxygen (0-21%) and propane concentrations (0-2%) with a total flow rate of 300 sccm. For sensor signal collection, a bias voltage is applied to the microheater and the resistance is measured with a Keithley 2602 source-meter. Sensor response is reported as  $(R-R_0)/R_0 \times 100\%$  where  $R_0$  is the average resistance in air and  $R$  is the average resistance during exposure to a given concentration of propane. Sensor testing is performed in synthetic air to control the oxygen concentration. A microheater operating temperature of 500 °C gives the best sensitivity while remaining in the linear TCR window of the polysilicon (Figure 7). Because the lower explosive limit of propane in air is 21,000 ppm or 2.1% [118], tests are performed with gas concentrations from 5,000 to 20,000 ppm. Sensor tests performed with bare BN showed no response to propane.

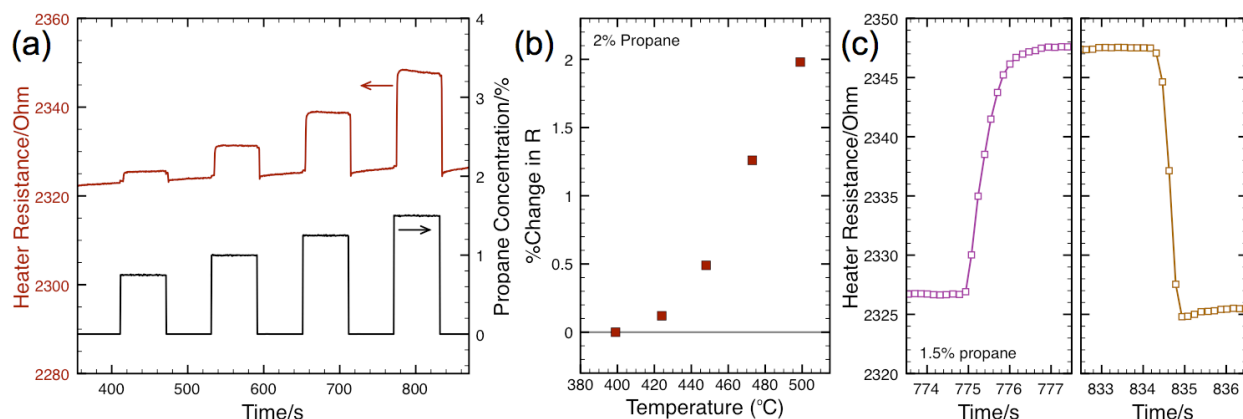


**Figure 7.** Microheater resistance versus temperature showing a linear range between 350 and 550 °C with thermal coefficient of resistance of 290 ppm K<sup>-1</sup>. Line is linear fit for the data points between 350 and 550 °C ( $R^2 = 0.9978$ ) and the slope is used to calculate the TCR.

#### 4. Propane sensing performance

Sensor testing is performed using propane gas as a representative combustible gas, because it is a commonly used hydrocarbon in heating, cooking, power generation, oil recovery [114], [115], and even refrigeration [116], [117]. When the sensor is exposed to propane gas in air, combustion of propane on the surface of the platinum nanoparticles releases heat, which increases the temperature and the resistance of the polysilicon microheater, since it has a positive thermal coefficient of resistance or TCR of 390 ppm K<sup>-1</sup> in the operating temperature range.

The low density and high thermal conductivity of BN enables superior catalytic gas sensing performance in terms of response and recovery time and sensor power consumption. The Pt-BN sensor resistance over time shown in Figure 8a exhibits low noise and fast response and recovery through range of propane concentrations tested. Because boron nitride has a high thermal conductivity, heat generated during propane combustion can be efficiently transferred to the microheater and raise its temperature. Additionally, the low density and high surface area means a minimized mass of the support material within a given volume so less of the heat generated in the exothermic reaction will go to heating the support. Graphene aerogel has similar advantages of surface area and thermal conductivity and performs well for hydrogen sensing [110], but methane and other lower alkanes require higher catalyst temperatures for detection (~500 °C), which is above the long-term thermal stability range for graphene aerogel (see Figure 1c). The Pt-BN sensor does not respond to propane at all below 400 °C and the sensor response increases with increasing temperature up to 500 °C (Figure 8b). Closer analysis of the data in Figure 8a shows the average time to reach 90% of the full sensor response ( $t_{90}$ ) is only 1.35 s for the response and 0.6 s for the recovery (Figure 8c shows a closer view of the response and recovery for 1.5% propane as a sample). In comparison, commercial products and reports from literature using a porous alumina support have shown response times from 10 to 20 s [15], [108], [155].



**Figure 8.** (a) Pt-BN sensor resistance when exposed to varying propane concentrations showing stable, fast response. (b) Pt-BN sensor response to 2% propane at different microheater temperatures. (c) Sensor response and recovery shown in close up for 1.5% propane exposure.

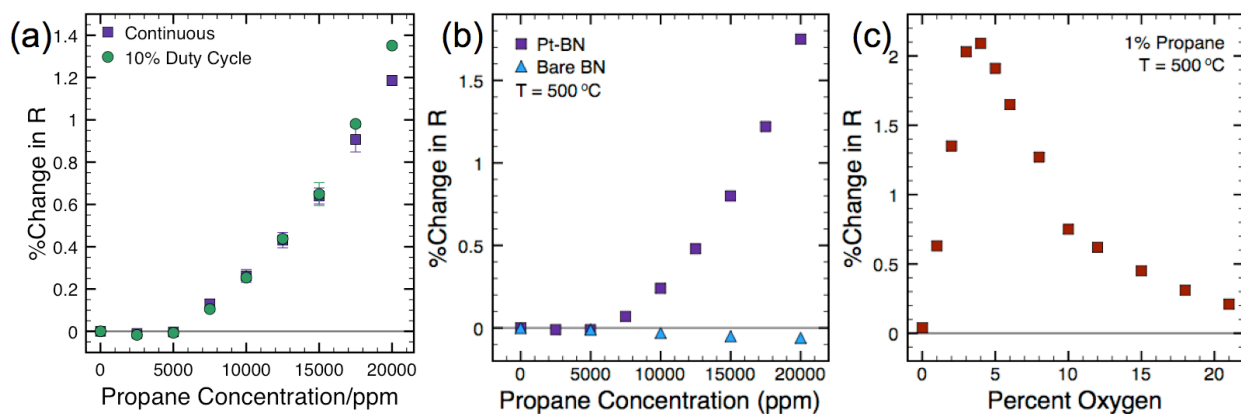
The sensitivity of the Pt-BN is competitive with commercially available products and other literature reports. In practical application, two microheaters are placed in a Wheatstone bridge configuration with one coated in catalytic material and one coated with bare support. Sensitivity is therefore reported as the change in voltage between the reference and active sensor (mV per % propane). Using the response of the bare BN to represent the reference sensor and the Pt-BN to represent the active sensor, we calculate a sensitivity of 15 mV per % propane, which is competitive with commercial MEMS pellistors at 12 mV per % [108]. The limit of detection of 5,000 ppm (Figure 9a) is comparable to other propane sensors in the literature [15], [108] and is determined by the signal to noise ratio of the temperature detector. Improvements to the limit of detection may be made with the addition of separate temperature detection channel on the microheater platform using a material with a larger TCR, like platinum, or by decreasing the size of the platinum nanoparticles to have more active surface area exposed per volume of aerogel. It is well known that the sensitivity of the catalytic gas sensor depends on the active catalytic surface area. Prior work has demonstrated that a thin film of platinum has lower sensitivity compared to platinum nanoparticles on a porous support [15].

The sensor power consumption also benefits from this fast response and recovery, as it makes duty cycling of the microheater possible. Figure 9a shows the sensor response versus propane concentration for continuous heating and for 100 ms every second, thereby reducing the average power from 15 to 1.5 mW without compromising response magnitude or measurement frequency. Single mW power consumption represents a two order of magnitude reduction from commercially available catalytic gas sensors [155]. Along with minimizing power requirements, cycling the microheater through various temperatures can also allow for selective measurement of combustible gases. Each combustible gas has a unique response curve over a range of temperatures and if this is well-characterized for a set of gases in a mixture of interest, measurements collected from the catalytic gas sensor at various temperatures can be analyzed to give single component response [29].

In order to confirm the sensing mechanism, several control experiments have been conducted. Figure 9b compares the average sensor response for a given propane concentration of a sensor made with bare BN, and the Pt-BN sensor. No response is seen without the presence of catalytic Pt nanoparticles. Although the auto-ignition temperature for propane is 450 °C [118], heating the bare microheater to 500 °C does not result in a sensing response. The heated area is too small to appreciably heat the surrounding gas and cannot create the conditions for auto-ignition. The overall expected chemical reaction of the propane combustion is



Figure 9c shows how the sensor response to propane (10,000 ppm or 1%) varies with the percentage of oxygen between 0 and 21%. The maximum response occurs at the stoichiometric ratio (5% O<sub>2</sub> for 1% C<sub>3</sub>H<sub>8</sub>), which is supported by catalysis research on propane oxidation by platinum catalysts [156], [157]. Competitive adsorption of oxygen on the platinum surface that limits the access of propane molecules is the suggested reason for the decrease in catalytic activity with increasing oxygen to propane ratio [156].

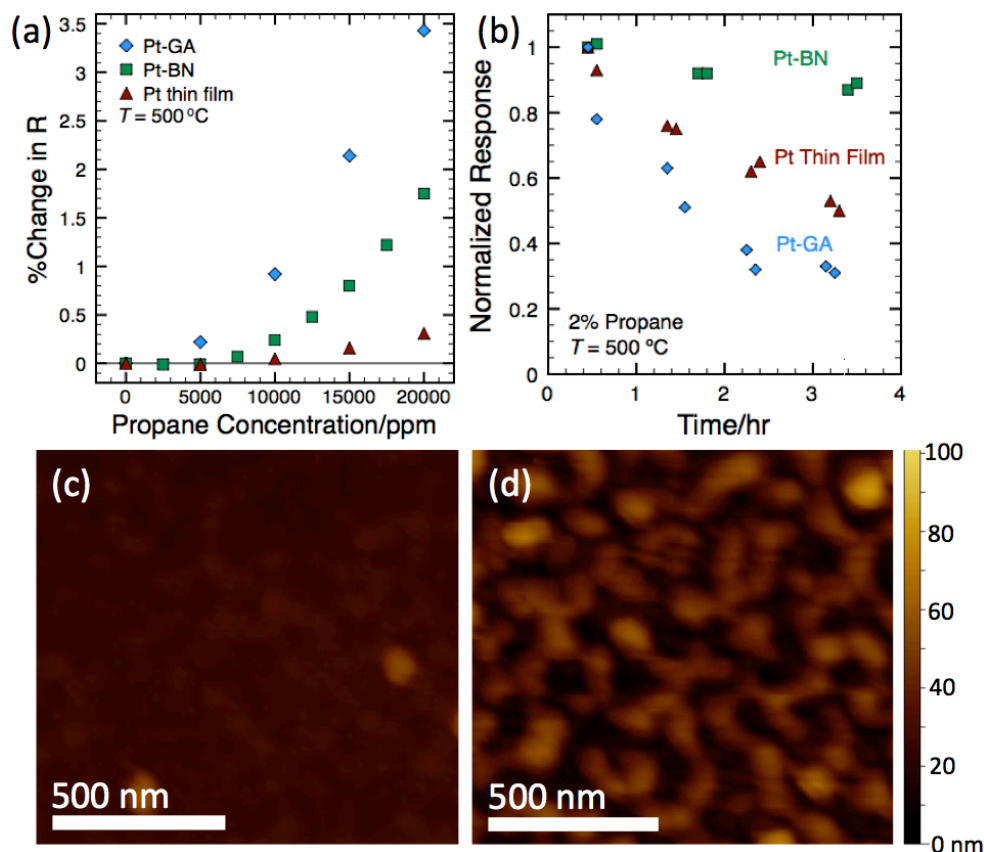


**Figure 9.** (a) Response of Pt-BN sensor versus propane concentration while heated to 500°C continuously (squares) and for 100 ms every second (circles), which lowers the overall power consumption to only 1.5 mW. (b) Comparison of sensor response at varying propane concentrations in synthetic air for Pt-BN and bare BN showing the necessity of the platinum to catalyze the propane reaction. (c) Response to propane (1% or 10,000 ppm) with changing oxygen concentration showing a maximum at the stoichiometric ratio of oxygen to propane (5 to 1). Each data point is the average of four exposures at that concentration over a three-hour test and the error bars are the standard deviation.

Stable, reproducible sensor performance relies both on the stability of the boron nitride support and the platinum nanoparticles. Previous works using BN as a catalyst support have suggested that the high thermal conductivity of BN improves the catalyst lifetime by dissipating heat generated in oxidation reactions and preventing the buildup of hot spots that can cause serious nanoparticle sintering [148], [158]. As discussed with Figure 5, high temperature treatment of the Pt-BN does not result in an increase in platinum nanoparticle size over 24 hours at 500 °C. To determine whether this stable Pt nanoparticle size on the BN aerogel translates to more stable catalyst performance, Pt-BN sensors were tested for several hours and compared to sensors fabricated with other forms of Pt. Figure 10 compares the response of Pt-BN sensors to sensors



made with platinum nanoparticle-loaded graphene aerogel (Pt-GA) and an evaporated Pt thin film. To make the evaporated Pt thin film sensor, silicon dioxide (20 nm) and platinum (6 nm) are thermally evaporated (Thermionics VE-100 Vacuum Evaporator) onto the microheater chip with one set of wire-bond pads physically masked. The silicon dioxide prevents the platinum thin film from creating a shorting path between microheater contacts.

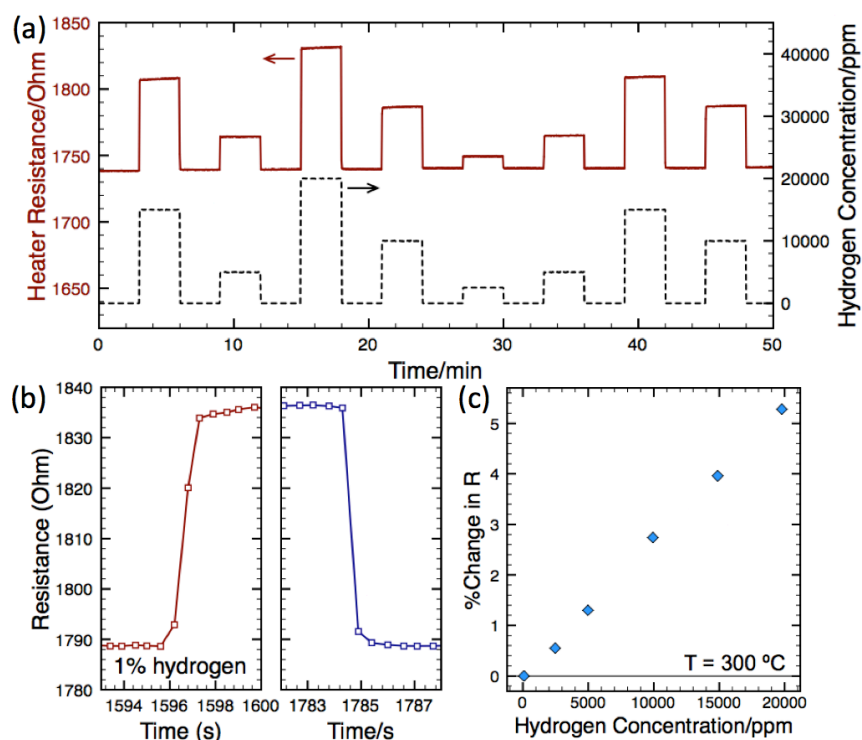


**Figure 10.** (a) Initial sensor response to varied propane concentration for the Pt-GA, Pt-BN, and evaporated Pt thin film showing sensitivity scaling with surface area. (b) Normalized response to propane (2% or 20,000 ppm) vs. time for Pt-BN, Pt-GA, and an evaporated Pt thin film, showing the enhanced stability of the Pt-BN sensor. AFM images of platinum thin film (c) as evaporated (RMS = 1.62 nm) and (d) after 6 hours of high temperature testing (RMS = 12.18 nm) showing film agglomeration (Z-range of 100 nm in both images).

In Figure 10a, it is evident that the Pt-GA sensor exhibits the highest sensitivity to various concentrations of propane initially, but Figure 10b shows that the response drops off rapidly over 4 hours. Figure 10b shows the sensor response to a propane concentration of 20,000 ppm, with the responses normalized to each sensor's initial value for clarity. The evaporated Pt thin film exhibits the lowest sensitivity, even though it is in closest contact to the heater. This demonstrates the benefit of the high surface catalyst support in increasing the active catalytic area. The response of the Pt-BN sensor is more sensitive than the evaporated Pt thin film and is significantly more stable than both the Pt-GA and the Pt thin film, with only a 14% decrease over

18 hours of operation. Atomic force microscopy (AFM, Digital Instruments NanoScope IIIa, tapping mode) of the platinum thin film, shown in Figure 10b and 10c, reveals that the film undergoes agglomeration during high temperature testing. Optical analysis of the Pt-GA after four hours of testing shows a loss of material that can be attributed to the graphene aerogel support burning off, as shown in Chapter 4. The enhanced thermal stability provided by the BN aerogel combined with the high surface aerogel structure gives this material the optimal combination of sensitivity and stability.

The Pt-BN sensor is also exposed to various concentrations of hydrogen gas with the microheater at a temperature of 300 °C. Figure 11 shows fast response and recovery and great sensitivity, comparable to that of Pt-GA as shown in Chapter 3. This shows that the use of boron nitride aerogel adds benefit for high temperature operation for propane combustion without losing the superior hydrogen sensing capabilities seen with Pt-GA.



**Figure 11.** (a) Resistance of Pt-BN sensor over time with various hydrogen concentrations. (b) Response and recovery of Pt-BN sensor to 1% or 10,000 ppm hydrogen. (c) Sensitivity of Pt-BN sensor to hydrogen. Microheater operated at 300 °C during (a), (b), and (c).

## 5. Conclusion

In summary, a high surface area, highly crystalline boron nitride aerogel synthesized with non-hazardous reactants has been loaded with crystalline platinum nanoparticles to form a novel nanomaterial that exhibits many advantages for use in a catalytic gas sensing application. Platinum nanoparticle-loaded boron nitride aerogel integrated onto a microheater platform allows for calorimetric propane detection. Boron nitride aerogel exhibits thermal stability up to 900 °C and supports disperse platinum nanoparticles, with no sintering observed after 24 hours of high

temperature testing. The high thermal conductivity and low density of the boron nitride aerogel results in an order of magnitude faster response and recovery times ( $<2$  s) than reported on alumina support and allows for 10% duty cycling of the microheater with no loss in sensitivity. The resulting 1.5 mW sensor power consumption is two orders of magnitude less than commercially available catalytic gas sensors and unlocks the potential for wireless, battery-powered catalytic gas sensing. The approach presented in this paper can be extended to nanoparticle loading of metals other than platinum, allowing improved performance for other hydrocarbon sensing.

## Chapter 6. Robust Catalytic Gas Sensing Using Highly Stable Silicon Carbide Microheaters<sup>5</sup>

### 1. Motivation

Combustible gases such as hydrogen and hydrocarbons are prevalent in industrial environments. More ubiquitous atmospheric monitoring of these gases would allow for faster leak detection, which would result in increased worker safety and reduced damage to equipment and the environment. However, installation of a fixed gas monitor in a class 1 or 2 hazardous facility can be very expensive. Wireless, battery-powered gas monitors would eliminate the bulk of the installation costs, but have power constraints that current combustible gas sensing technology cannot meet. Development of a low-power catalytic sensor with competitive performance characteristics is the critical step in allowing for ubiquitous combustible gas monitoring.

The main reason for the high power consumption of current sensor components is the need for the catalyst to be heated to high temperatures ( $\sim 500^\circ\text{C}$ ). To minimize the power consumption, two main strategies have been proposed: (1) miniaturization through the use of microfabricated heaters, and (2) reducing the combustion temperature. Research efforts on efficient low-temperature hydrocarbon combustion has not yielded promising results [8], [15]; thus research focus has been on the use of microheaters as the catalytic gas sensor platform [9], [15], [16], [109]. A microfabricated sensor platform can leverage silicon micromachining processes for low cost and reproducible manufacturing. Microheaters have been fabricated from a variety of materials, most commonly polycrystalline silicon (polysilicon) or platinum, and consist of a heater trace thermally isolated from the substrate via a thin membrane of silicon nitride or silicon dioxide. Joule heating is used to reach the desired operating temperatures.

Although progress has been made in minimizing the power consumption of these microheaters, deployment of microheater-based catalytic gas sensors is contingent on obtaining stable, reproducible measurements in field conditions. Platinum and polysilicon microheaters both suffer from instability when operated at the high temperatures required for catalytic gas sensing. Platinum suffers from electromigration, poor adhesion to the most common membrane materials [20], [61], and oxidation if it is not isolated from the atmosphere. The resistance of polysilicon is not very stable as it approaches the recrystallization temperature ( $\sim 600^\circ\text{C}$  [77]), where grains can coalesce and cause long-term drift [77], [159], [160]. Especially considering that  $500^\circ\text{C}$  is the baseline operating temperature and the temperature increases in the presence of combustible gas, these materials suffer severe drawbacks for long-term use.

Silicon carbide (SiC) has been investigated as an advantageous material for microelectronics and microsensors involving high temperature operation [161], [162]. The robust performance of SiC at high temperature makes it an attractive replacement for polysilicon [161]. Silicon carbide has been used in microheater fabrication, both as a membrane material since its high thermal conductivity leads to better temperature uniformity across the device [163]–[167], and as the

---

<sup>5</sup> A modified version of this work was published in A. Harley-Trochimczyk, A. Rao, H. Long, C. Carraro, R. Maboudian, “Robust Catalytic Gas Sensing Using a Silicon Carbide Microheater,” Proceedings of the 2016 Solid-State Sensor and Actuator Workshop, Hilton Head ’16.

microheater material [162], [164], [168]–[171]. SiC microheaters have demonstrated robust behavior in high temperature applications [162], [171], including for metal oxide-based gas sensing [165], but their use for catalytic gas sensing is not reported to-date.

**Table 1.** Thermal properties of various microheater materials

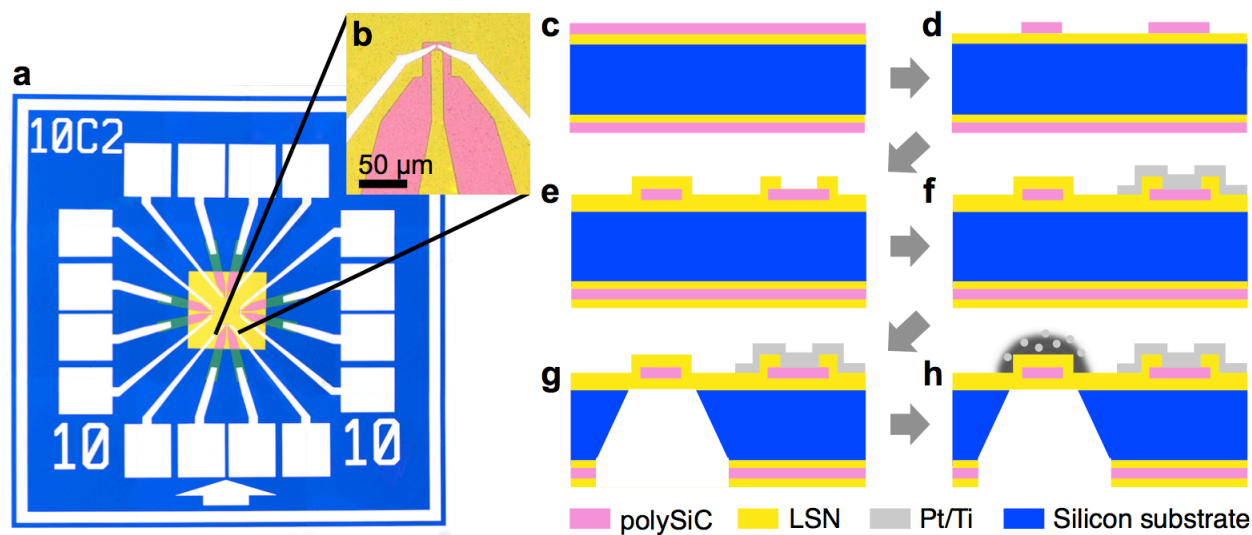
|                                                           | Polysilicon | Silicon Nitride | 3C-Silicon Carbide            |
|-----------------------------------------------------------|-------------|-----------------|-------------------------------|
| Melting Temperature (°C)                                  | 1414 [62]   | 1900 [172]      | 2730 (sublimation point) [62] |
| Thermal coefficient of expansion (ppm K <sup>-1</sup> )   | 2.8 [173]   | 2.4 [173]       | 6 [62]                        |
| Thermal conductivity (W m <sup>-1</sup> K <sup>-1</sup> ) | 18-29 [173] | 20-30 [173]     | 120 [62]                      |

Here the development of a low-power silicon carbide microheater, requiring only 20 mW to reach 500 °C, is reported. Comparison of the SiC microheater to a polysilicon microheater with the same dimensions shows significant improvements in baseline resistance stability for operation at 500 °C and above. With the integration of an advanced catalytic material, platinum nanoparticle-loaded boron nitride aerogel, the SiC microheater platform can be used for propane detection with high sensitivity, fast response and recovery (<1 s) and highly stable response. Additionally, the sensitivity is unaffected by humidity and by 10% duty cycling, which lowers the power consumption to only 2 mW with data still collected every two seconds. These developments offered by the SiC microheater can unlock the true potential of low power catalytic gas sensing for wireless applications.

## 2. Microheater fabrication and testing

### 2.a. Silicon carbide microheater fabrication

The microheater platform consists of a back-etched silicon nitride membrane encapsulating four microheater elements on a single chip that is 3.5 x 3.5 mm<sup>2</sup> in size (Figure 1a). The thin membrane provides the microheaters with thermal isolation from the substrate to keep the power consumption low requiring only 20 mW to reach 500 °C. Because the silicon nitride layers are optically transparent, the encapsulated SiC trace (pink) can be seen in Figure 1b. The two Pt/Ti sensing electrodes (white) are not used in this work and are masked with a thin layer of silicon dioxide before sensor testing to avoid interference from the platinum. The hot zone is the narrowest part of the trace, giving an approximately 50 x 50 μm<sup>2</sup> heated area. Figure 1h shows a cross-sectional schematic of the microheater with the closed membrane configuration and metal contacts placed off the membrane to keep them cool and hence, avoid stability issues associated with metal contacts at elevated temperatures. The closed membrane assists with integration of the sensing material by providing a flat surface for deposition.



**Figure 1.** (a) Optical image of four SiC microheaters on the chip ( $3.5 \times 3.5 \text{ mm}^2$ ) and (b) close-up of one microheater. (c-h) Overview of microheater fabrication process. (c) Low pressure chemical vapor deposition of a low-stress silicon nitride (LSN) layer and doped SiC layer. (d) polySiC is patterned and etched to form the microheaters. (e) A second LSN layer is deposited to encapsulate the microheaters and a window is etched in the top LSN layer. (f) Pt/Ti metal contacts are created through photolithography, evaporation, and lift-off. (g) A window is etched in the back-side of the wafer to expose the silicon substrate, which is anisotropically etched with hot KOH to release the membrane. (h) Catalytic material is deposited on the microheater for catalytic gas sensing.

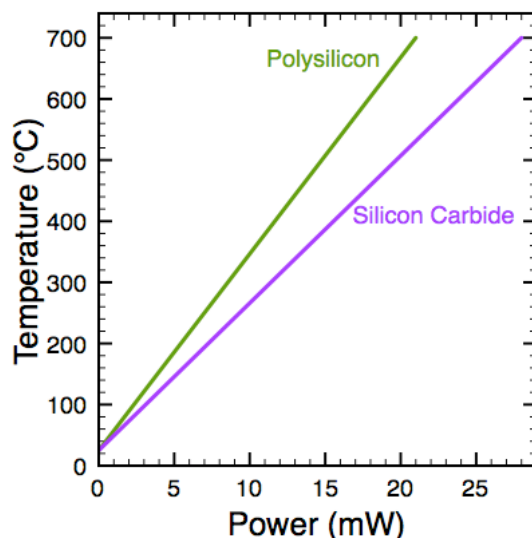
The silicon carbide fabrication process follows the previously developed polysilicon microheater fabrication, described in detail in Chapter 2. To facilitate comparison, only the deposition and etch chemistries for the silicon carbide steps are changed. Briefly, the deposition of 100 nm low-stress silicon nitride (LSN) film layer on a 4-inch p-type double-side polished silicon wafer is followed by the silicon carbide film deposition (Figure 1c). The SiC film is deposited using methylsilane (30 sccm), hydrogen (48 sccm), and dichlorosilane (15 sccm) as precursors in a low-pressure (170 mTorr) hot-wall reactor (*tystar15*, recipe 15CH6SIA, 25 minutes) at  $T = 835^\circ\text{C}$  with a dopant source of ammonia gas (3 sccm) and with the wafers in a closed-boat geometry with slots to limit the gas diffusion and improve the film uniformity [174]. The deposited film is polycrystalline cubic 3C-SiC with a thickness of 130 nm and a sheet resistivity of  $5,700 \Omega$  per square (measured using an automatic 4-point probe tool, *cde-resmap*). The SiC film thickness, when multiple thin films are involved, can be difficult to determine using *nanospec*; thus, for a more accurate measurement, the bottom silicon nitride layer thickness is measured with *nanospec* the SiC deposition and then again in an area where the nitride is exposed after the SiC etch. In conjunction with profilometry (*asiq*) to measure the silicon carbide feature height, the difference in silicon nitride layer thickness (the overetch) subtracted from the step height yields the silicon carbide film thickness.

To define the microheaters (Figure 1d), the wafer is patterned with photolithography employing positive photoresist (FujiFilm OiR 906-12) with a thickness of  $\sim 1.2\ \mu\text{m}$  as the mask. To selectively remove the SiC, reactive ion etching is done with HBr and  $\text{Cl}_2$  gases using a transformer coupled plasma system (*lam8*) [175]. A high power of 300 W is needed to have an appreciable etch rate ( $\sim 1.5\ \text{nm s}^{-1}$ ), hence the etching is done in 10 s increments to prevent overheating of the photoresist mask. The *lam8* etcher only takes 6-inch wafers, so the 4-inch wafers must be mounted on a 6-inch carrier wafer for processing. To do so, the carrier wafer is heated on a hotplate at  $120\ ^\circ\text{C}$  for a minute, then a small drop of vacuum oil is put in the center. The 4-inch wafer is placed on top, positioned roughly in the center, and heated for 30 minutes. To degas the oil, the wafer is placed in *technics-c* (clean the chamber first with oxygen plasma) and held at low pressure for 10 minutes (can also use *ptherm*, but that tool is in higher use). To remove the carrier wafer, it is placed on a hotplate at  $120\ ^\circ\text{C}$  and after a minute of heating, the 4-inch wafer can be removed and cleaned with acetone to remove the grease. After the wafers are cleaned, a second silicon nitride layer with a thickness of 100 nm is deposited to encapsulate the microheaters and windows are etched to allow for metal contact to be made to the silicon carbide (Figure 1e). The metal contacts are defined through photolithography, evaporation of 90 nm Pt on a 10 nm Ti adhesion layer and lift-off with acetone with the same procedure as described in Chapter 2 (Figure 1f). Finally, a window is plasma-etched on the back-side of the wafer to expose the silicon substrate, which is etched in a KOH bath (24 wt%) at  $80\ ^\circ\text{C}$  with bubbled oxygen to release the membrane (Figure 1g). The front-side of the wafer is protected with an alkaline resistant coating (Brewer Science, Protek B3) during the KOH etch. The protective coating is kept in place during the dicing process and removed from individual chips before use.

## 2.b. Microheater testing

The microheater testing is done with a Keithley 2602A source-meter. The current-voltage measurements are taken with LabTracer 2.9 software. The continuous and variable temperature tests are taken with an open-source Java-based program called Zephyr. As discussed in Chapter 2, convection through the air is minimal with the small element size and radiative effects can be considered to be negligible at operating temperatures below  $700\ ^\circ\text{C}$ . Modeling conduction with Fourier's law gives a linear relationship between applied power and the temperature difference between the microheater and room temperature (Figure 2). Given the linear relationship between applied power and temperature, the temperature can be defined with two calibration points. The first is at room temperature and the second is done by powering the heater to the glowing point and then fitting the emission spectrum with a Planck distribution [79], [176]. The onset of visible glow is found to be  $\sim 700\ ^\circ\text{C}$  which is 21 mW for the polysilicon microheaters and 28 mW for the SiC heaters. Although measuring the heater resistance during external heating is a common temperature calibration technique, it is not accurate for this microheater platform because the colder parts of the heater contribute a non-negligible portion of the total resistance. Therefore, external heating where the entire chip is at a given temperature does not provide the same resistance as when only the hot zone of the microheater is at that temperature.





**Figure 2.** Temperature versus power relationship for the polysilicon and SiC microheaters.

### 3. Sensor fabrication and testing

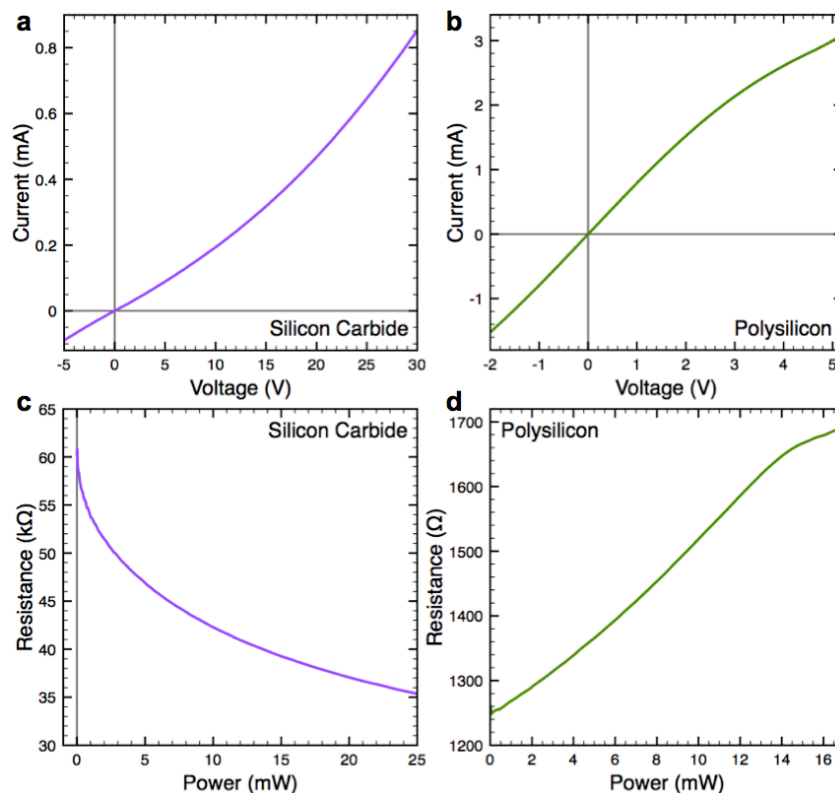
The platinum nanoparticle-loaded boron nitride aerogel (Pt-BN) synthesis can be found in full detail in Chapter 5. Scanning electron microscopy imaging is done with a Zeiss LEO 1550 system to observe the aerogel morphology. For sensor testing, an individual chip is wire-bonded into a ceramic dual in-line package. The Pt-BN is sonicated into suspension in isopropyl alcohol (IPA) and a few microliters are dropped onto the chip while the microheater is heated to the boiling point of IPA (80 °C) to facilitate local deposition. The packaged sensor is exposed to the gases of interest in a 1 cm<sup>3</sup> Teflon chamber. Propane (5% in N<sub>2</sub>, Praxair), oxygen, and nitrogen gas flow rates are set by a Labview program that controls Bronkhorst mass flow controllers. The oxygen content is controlled at 20% and the total gas flow rate is held to 300 sccm. A Keithley 2602A source-meter and Zephyr software are used to apply a given potential to the sensor and record the sensor resistance in response. Sensing response is reported as  $(R-R_0)/R_0 \times 100\%$  where  $R$  is the sensor resistance during exposure to a given concentration of gas and  $R_0$  is the sensor resistance in synthetic air only.

## 4. Results and Discussion

### 4.a Microheater characterization

The current-voltage sweeps of the SiC and polysilicon microheaters are shown in Figure 3a and 3b. The resistance versus power relationship is calculated from the current-voltage sweep and plotted in Figure 3c and 3d. Because the power is linearly proportional to the heater temperature in the range up to 700 °C, the resistance-power relationship is the same as the resistance-temperature relationship. The SiC microheaters have a higher resistance at room temperature, about 60 kΩ compared to 1.25 kΩ for the polysilicon microheaters. The SiC microheaters require a higher applied voltage to reach the same power as the polysilicon microheater, which is the reason for the potential sweep extending to 30 V compared to 5 V for polysilicon. To reach 500 °C, the polysilicon microheater requires 15 mW while the SiC microheater requires 20 mW, which is attributable to the higher thermal conductivity of SiC compared to polysilicon [161].

With a higher thermal conductivity, the silicon carbide trace can sink more heat into the substrate, lowering the heating efficiency or power required to reach a given temperature.

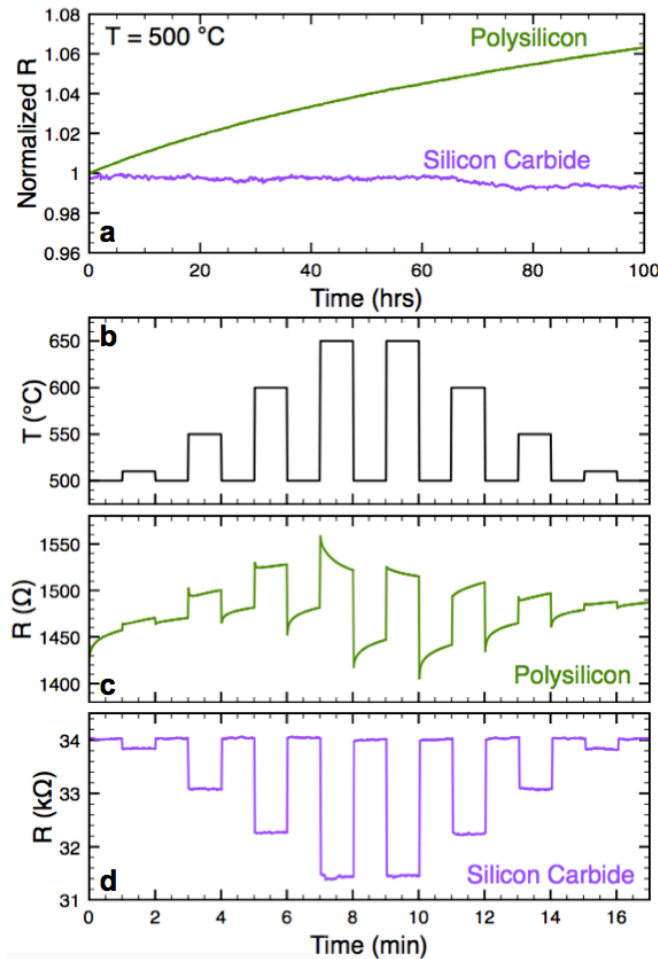


**Figure 3.** Current-voltage sweeps for (a) SiC and (b) polysilicon microheaters. Resistance versus power relationship calculated from the current-voltage sweep for (c) SiC and (d) polysilicon microheaters.

As is evident from Figures 3c and 3d, the two microheaters have temperature coefficients of resistance that are opposite in sign and non-linear, with the polysilicon resistance increasing with temperature and the SiC resistance decreasing with temperature. With the heater at 500 °C, the calculated TCR values are +350 ppm K<sup>-1</sup> for polysilicon and -700 ppm K<sup>-1</sup> for SiC. The magnitude and sign of the SiC TCR are comparable to prior reports [169], [177]. The sign of the microheater TCR is controlled by the competing effects of increased phonon scattering in the crystal grain leading to an increasing resistance with temperature, and thermal activation of carriers through the grain interfaces leading to a decreasing resistance with temperature. The change in slope observed in polysilicon at 14 mW coincides with the recrystallization temperature. Because the magnitude of the SiC TCR is twice as large as the polysilicon, the same change in temperature due to gas combustion results in a larger resistance change from SiC than from polysilicon, making it a more sensitive transducer for catalytic gas sensing.

Figure 4a shows a plot of microheater resistance when heated at 500 °C versus time. The resistance of each microheater is normalized to the initial value for easier comparison. When both microheaters are powered for 100 hours, the SiC microheater shows an order of magnitude lower drift (-0.6%) than the polysilicon (7%). The SiC microheater displays a higher noise level,

possibly due to the lower current level used to reach the operating temperature. Previous reports have shown long-term positive resistance drift of polysilicon microstructures at temperatures close to 500 °C [77], [159], and suggested the cause may be dopant diffusion along the temperature gradient or dopant segregation at grain boundaries. Some decrease in the rate of drift is observed over the first 100 hours, suggesting that with a long “burn-in” or conditioning time, the drift could be mitigated. However, during catalytic gas sensing, the combustion of the target gas leads to an increase in temperature above the 500 °C baseline; thus the microheater behavior with must be stable changing high temperature as well as with a constant baseline.



**Figure 4.** (a) Normalized resistance of SiC and polysilicon microheaters continuously powered to 500 °C for 100 hours. (b) Temperature profile applied to the microheaters and resulting (c) polysilicon and (d) polySiC microheater resistance.

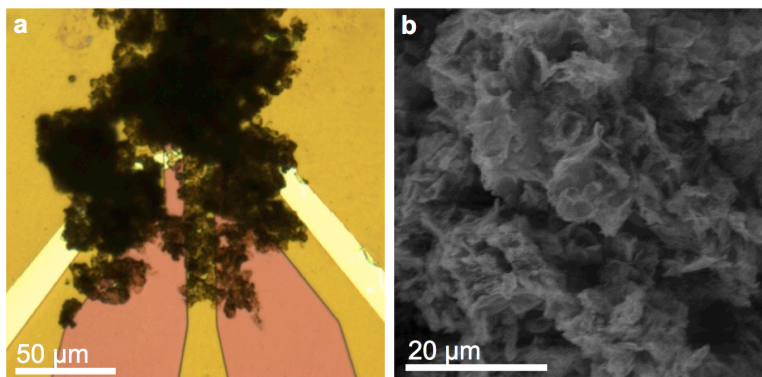
To demonstrate this issue, applying a set of temperature changes from 510 to 650 °C with a baseline of 500 °C (Figure 4b) results in major instability in the polysilicon microheater, including history dependence (Figure 4c) where the response depends on what temperatures are previously reached. The recrystallization temperature of polysilicon is around 600 °C [77]; thus the resistance decrease when the microheater is held at the highest temperature may be due to grain growth. During the return to baseline, the resistance increases again just as with the long-

term drift observed in Figure 4a. In a previous report, the resistance of a polysilicon heater at low temperature depends on the high temperature previously reached and the cooling rate [77]. In the temperature profile applied in Figure 4b, the temperature switching is done in the same length of time by with different temperature changes, so the cooling rate differs for each temperature reached. This may explain why the polysilicon microheater returns to different resistance values after reaching various elevated temperatures. In contrast to this unpredictable behavior, the SiC microheater displays stable baseline recovery even when heated to 650 °C (Figure 4d) as well as stable resistance values when the temperature is held constant at a particular value. The wide bandgap and high chemical stability of silicon carbide make it highly resistant to thermally induced resistance drift, which makes it the superior choice for a sensing platform with high operating temperature.

#### **4.b. Catalytic gas sensing performance**

With the addition of Pt-BN as the catalytic material (Figure 5a), the SiC platform can be used for catalytic gas sensing. Figure 5a shows the Pt-BN after drop-casting on top of the silicon carbide microheater. As a commonly used fuel, refrigerant, and process chemical, propane is used to demonstrate the sensor performance [114], [118]. Although the auto-ignition temperature for propane is 450 °C, there is no response from the bare microheater. Other researchers have shown that small microheater-based sensors are inherently explosion-proof without expensive packaging [108]. The lower explosive limit (LEL), defined as the lowest concentration capable of producing an explosion, for propane is 2.1% or 21,000 ppm; thus, the sensor is exposed to concentrations below that value. As shown in Chapter 5, the sensors made with bare boron nitride aerogel do not show any propane response, indicating the platinum nanoparticles are required for gas combustion.

The SEM image of the Pt-BN in Figure 5b shows the high surface area morphology of the material. The transmission electron microscopy analysis reported in Chapter 5 indicates that the average Pt nanoparticle diameter is 17 nm and the platinum is crystalline and well-adhered to the boron nitride aerogel. The platinum loading is 45 % by weight. Earlier analysis also shows that the boron nitride aerogel scaffold is 7-10 layers thick and the specific surface area is calculated to be 450 m<sup>2</sup> g<sup>-1</sup> before platinum loading using nitrogen adsorption [176]. The high specific surface area allows for high nanoparticle loading with minimal support mass, improving the transfer efficiency of the heat generated during hydrocarbon combustion and the response time. The boron nitride aerogel scaffold is chosen because of the improved thermal stability it gives over graphene aerogel.

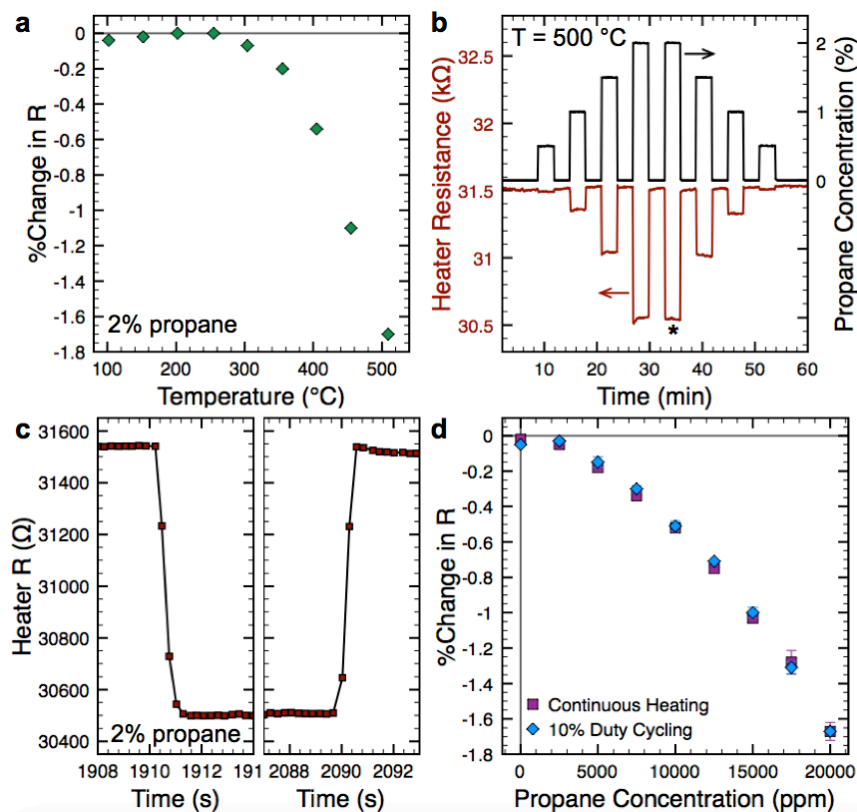


**Figure 5.** (a) Optical image of the Pt-BN catalyst after drop-casting on top of the microheater. (b) SEM image of the Pt-BN showing the high surface area morphology.

Figure 6a shows the effect of temperature on sensor response to 2% propane, where the response is defined as percentage change in resistance. The figure shows that above 300 °C, the propane response monotonically increases with temperature. Even at 500 °C, the sensor has not reached a mass-transfer limited regime, beyond which point the sensitivity is expected to not change as strongly with temperature. Operating in a kinetically-limited regime impacts the linearity of the response with concentration, because as the sensor responds and heats up, the rate of reaction increases, leading to further increases in temperature and rate. This explains the non-linearity seen in the response vs concentration curve in Figure 6b. Operating at higher temperatures in order to reach a mass-transfer limited regime is possible with the silicon carbide microheater, but the power consumption increases and above 700 °C, the relationship between power and temperature becomes non-linear as radiative heat loss increases, making it much more difficult to interpret the signal.

The Pt-BN SiC sensor resistance shown in Figure 6c with varied propane gas exposure shows a high degree of stability in the baseline and reproducibility in response. In between the propane exposures, clean, dry synthetic air is flown over the sample. Exposure to 2% propane results in an approximately 65 °C increase of the microheater temperature, as estimated from the resistance versus temperature calibration curve, but the sensor recovers well to the baseline after gas exposure. Using a signal-to-noise ratio of 3, the limit of detection is calculated to be 3,420 ppm propane at the operating temperature of 500 °C. Given that the lower explosive limit for propane is 21,000 ppm, the sensing range of the device is quite respectable and comparable to other literature reports for micropellistor-based propane detection [15], [108]. The sensor response is very fast, comparable to previous results using the polysilicon microheater [110], [176], [178]. Figure 6d shows a zoomed-in view of the starred response in Figure 6c for the start of exposure to 2% propane and the recovery when the gas is switched back to clean air. The times to reach 90% of the full signal level ( $t_{90}$ ) for response and recovery of the sensor are <1 s. In the quest for a battery-powered combustible gas sensor, decreasing the power consumption through duty cycling, or only powering the heater for short bursts, is a useful strategy. However, larger heater elements with a slower response time require infrequent data collection or do not reach the full operating temperature during duty cycling and the sensitivity suffers. Here, the heater is turned

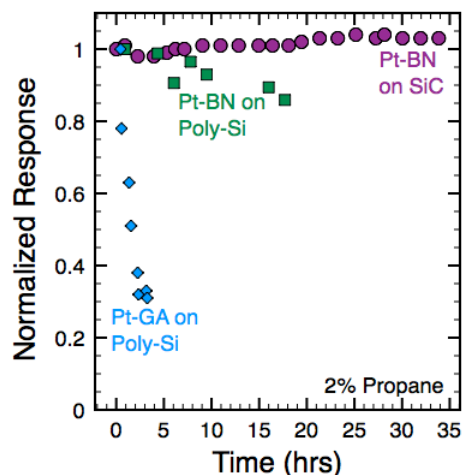
on for 200 ms every 2 s with no change in the sensitivity compared to continuous heating at 500 °C (Figure 6b) and the data collection remains at high frequency (every 2 s).



**Figure 6.** (a) Pt-BN SiC sensor response to 2% or 20,000 ppm propane at various operating temperatures. (b) Response to varied propane concentrations versus time at 500 °C showing good baseline stability and response reproducibility. (c) Pt-BN SiC sensor response and recovery time for 2% propane ( $t_{90} < 1$  s) at 500 °C (d) Sensitivity of the Pt-BN SiC sensor during continuous heating at 500 °C and 10% duty cycling with the heater on for 0.2 s every 2 s.

The increased stability of the microheater platform results in a propane sensor with improved response stability. As seen in Figure 7, the Pt-BN SiC sensor response is highly stable over a 36-hour period of extended continuous operation at 500 °C where the sensor is alternately exposed to clean air and various concentrations of propane. Figure 7 only shows the response to 2% propane for clarity, even though the sensor is exposed to varied concentrations during the test. The response stability is also compared to that of Pt-BN on a polysilicon microheater and platinum nanoparticle-loaded graphene aerogel (Pt-GA) on a polysilicon microheater. The graphene aerogel has been shown in Chapter 4 to burn off the microheater during testing, which explains the precipitous drop in response over only a few hours. The Pt-BN on polysilicon performs better but still shows a 15% change in the first 18 hours and no visible loss of material. The instability in the microheater resistance at the high operating temperature makes it difficult to fully interpret the behavior. As the heater voltage, rather than heater power, is held constant in these measurements, the polysilicon resistance changes with time at these temperature (Figure 4a), thus affecting the sensor response. In comparison, the Pt-BN SiC sensor shows no change in

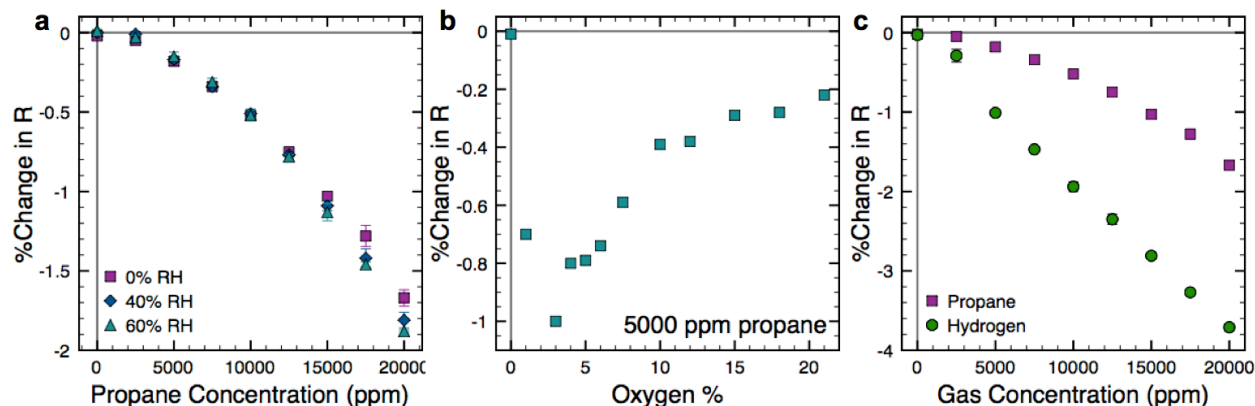
response over a period of 36 hours. For practical use, a stable sensor response would need to be demonstrated over a much longer time period, but even in the first 36 hours, the benefit of using silicon carbide as the microheater material is clear. In the same way that the choice of a more thermally stable aerogel material (boron nitride instead of graphene) improved the response stability on the same microheater platform, the choice of a more thermally stable microheater material (silicon carbide instead of polysilicon) demonstrates significant benefit for sensor reliability.



**Figure 7.** Pt-BN SiC sensor response to 2% propane over 36 hours of operation at 500 °C compared to Pt-BN, Pt-GA, and a Pt thin film on the polysilicon microheater.

The Pt-BN SiC sensor maintains good propane response when the relative humidity level is increased to 40 and 60% (Figure 8a). At the highest propane concentrations, the response is a bit higher as the humidity level increases. This may be a result of the lower effective oxygen concentration at higher humidity levels. As seen in Figure 8b, the sensor response to 5,000 ppm propane changes drastically with varied oxygen concentration. The largest response is around 3% oxygen, which is close to the stoichiometric ratio of oxygen to propane for complete combustion (5:1). The same behavior is reported in catalysis literature on propane oxidation by platinum catalysts [156], [157]. The suggested reason for the decrease in catalytic activity with an oxygen-to-propane ratio above the stoichiometric ratio is the competitive adsorption of oxygen on the platinum surface that limits the access of propane molecules [156]. In the presence of increased relative humidity, the effective oxygen concentration may be lower than the delivered 20%, which would lead to a slight increase in the sensor response. Functionally, this suggests that for accurate propane detection, the catalytic gas sensor must be paired with an oxygen sensor. However, for a simple alarm for leak detection, an increased propane concentration displaces some of the oxygen, giving a larger sensor response as the leak worsens.





**Figure 8.** (a) Pt-BN SiC sensor response to propane at 500 °C with varying levels of relative humidity. (b) Sensor response to 5,000 ppm propane with varied oxygen concentration. (c) Comparison of Pt-BN SiC sensor response to propane and hydrogen.

In addition to propane, the Pt-BN SiC sensor also responds to hydrogen gas (Figure 8c). The sensitivity for hydrogen is larger than propane even though the combustion energy per mole of gas is lower. This is probably due to the faster reaction kinetics. For some catalytic gas sensing applications, this lack of selectivity may be allowable, as the sensor warns of any potential combustible gas. To improve the selectivity, it is possible to measure the sensor response at various operating temperatures and using analysis such as principal component analysis, determine the contribution of each gas in the mixture to the total response [179]–[181]. Each gas has a unique response curve with temperature; for example, hydrogen gas has a high response starting at temperatures of 300 °C. The fast thermal response of the microheater can allow for rapid scanning through various operating temperatures.

## 5. Conclusions

Catalytic gas sensors with low power consumption are possible with a miniaturized microheater platform, but stable and reliable performance is critical for practical use. This chapter shows that changing from a polysilicon microheater to one fabricated with polycrystalline silicon carbide yields improved performance during high temperature operation. The SiC microheater retains a low power consumption (20 mW for 500 °C) and a high temperature coefficient of resistance, which is important for sensing. It also shows much more stable resistance during continuous heating at 500 °C and during temperature changes from 500 °C up to 650 °C when compared to the polysilicon microheater platform. When a thermally stable catalytic material (in this case, platinum nanoparticle-loaded boron nitride aerogel) is added, the SiC microheater element acts as a catalytic gas sensor element with good sensitivity and response stability for propane detection. Fast response and recovery time (<1 s) is demonstrated, as well as minimal impact to the sensitivity in a humid environment. With no loss in sensitivity during 10% duty cycling, the power consumption can be decreased to 2 mW with data still collected every 2 s. Even within the same microheater design, the choice of heater material can have a large impact on the performance of the catalytic gas sensor. The improved reliability of the SiC-based catalytic gas sensor makes wireless monitoring of combustible gases much more practical and feasible.

## Chapter 7. High Surface Area Graphene and Graphene Hybrid Aerogels for Ultrasensitive Gas Detection<sup>6</sup>

### 1. Motivation

In previous chapters, the benefits of graphene aerogel as a catalyst scaffold are elucidated, from the high specific surface area that allows high catalyst loading with minimal support mass to the high thermal conductivity that allows for more efficient heat transfer. However, graphene has also attracted much attention in recent years as a potential material for advanced electronic devices [39], [40]. Since the first report of its exceptional physical properties such as high carrier mobility and excellent mechanical strength [182], graphene has been investigated as a potential chemical sensing material. In fact, single-layer graphene has been shown to exhibit excellent sensitivity to gases, at the single molecule level, thanks to its high surface to volume ratio, high electrical conductivity and low noise [42], [43], [183]. The conductance of the graphene changes with the direct adsorption of the gas species on the surface, so the sensing measurement is based on measuring a resistance change in the graphene sensing film. However, graphene-based sensors have slow response and recovery times when used at room temperature, which greatly hinders their practical use [48]–[50], [53], [54], [184]–[188]. Faster response and recovery can be achieved by heating the sensing material, which increases the desorption rate of the adsorbed species. In order to keep the sensor power consumption low, a microfabricated heater is used for the heating [51], [54], [97], [110], [176], [189]. But integration of single-layer materials onto a microfabricated heater platform can be difficult and the surface area is limited to the heater footprint. The assembly of 2D sheets into a three-dimensional aerogel structure opens up new opportunities for enhanced sensing properties by maintaining a high surface area in an accessible porous network [100], [102], [190]. The same graphene aerogel used as a catalyst scaffold can itself act as a gas sensing material, with high surface area per footprint and good electrical conductivity as well as thermal conductivity.

Because the sensing mechanism relies on charge transfer between the sensing material and the adsorbed target gas, conductometric sensing using graphene is most useful for target gases that are strong electron donors or acceptors. Therefore, in order to probe the conductometric sensing properties of the graphene aerogel, nitrogen dioxide is used as an electron accepting gas and carbon monoxide and hydrogen are used as electron donating gases. Nitrogen dioxide (NO<sub>2</sub>), one of the most common and toxic air pollutants from combustion and automotive emissions, can cause serious diseases such as chronic bronchitis, emphysema, and respiratory irritation at low concentrations (53 ppb as set by the United States Environmental Protection Agency [191]). Carbon monoxide (CO) is another common and toxic exhaust gas, in this case with a permissible

---

<sup>6</sup> A modified version of this work has been published as H. Long, A. Harley-Trochimczyk, T. Pham, Z. Tang, T. Shi, A. Zettl, C. Carraro, M. A. Worsley, R. Maboudian. “High surface area MoS<sub>2</sub>/graphene hybrid aerogel for ultrasensitive NO<sub>2</sub> detection,” *Advanced Functional Materials*, DOI:10.1002/adfm.201601562

exposure limit of 50 ppm [192]. As discussed in Chapter 3, hydrogen is dangerous due to its flammability with a lower explosive limit of 4% or 40,000 ppm in air [89]. Commercially available conductometric sensors for these gases tend to have high power consumption that limits their use in battery-powered wireless monitoring applications. The combination of the microheater platform and the aerogel should allow for low power with a high sensitivity given the high accessible surface area per device footprint.

One challenge for graphene-based sensors is their poor selectivity without proper surface modification [42], [43], [51], [183], [193], [194]. More recently, layered transition-metal dichalcogenides, such as molybdenum disulfide ( $\text{MoS}_2$ ), are being explored as promising alternatives to graphene-based systems for many device applications [195]. Single or few-layer  $\text{MoS}_2$  sheets have been used in field effect transistor gas sensor devices for gases such as nitrogen dioxide and ammonia [49], [53], [54], [186], [187]. Previous efforts to construct aerogels from  $\text{MoS}_2$  sheets resulted in a fairly low specific surface area ( $18 \text{ m}^2 \text{ g}^{-1}$ ) [196], especially compared to that of graphene aerogel ( $1200 \text{ m}^2 \text{ g}^{-1}$ ) [100]. A hybrid aerogel with a graphene scaffold coated in single- to few-layer  $\text{MoS}_2$  nanosheets leverages the complementary properties of the two materials [196]–[198]. For conductometric sensing purposes, the graphene scaffold allows for lower noise measurements than  $\text{MoS}_2$  alone, since  $\text{MoS}_2$  is much less conductive than graphene [196]. Furthermore, the thermal conductivity of graphene is much higher than  $\text{MoS}_2$  ( $5000$  vs.  $35 \text{ W m}^{-1} \text{ K}^{-1}$  for single layer [101], [199]), thus the graphene scaffold can efficiently and quickly distribute heat from the microheater platform to the  $\text{MoS}_2$  sheets. The 2D structure of the  $\text{MoS}_2$  sheets on graphene not only increases the contact area for efficient charge transfer across the interface, but also shortens the charge transport time and distance, thereby improving the device performance [195], [197], [198]. 3D  $\text{MoS}_2$ /graphene hybrid structures have been investigated for hydrogen evolution catalysis [196], [198], [200]–[202], supercapacitors [203], lithium storage [204], and DNA sensing [205]. To date, the use of  $\text{MoS}_2$ /graphene hybrid structure for gas sensing has not been reported.

Here, the use of high surface area graphene aerogel for conductometric sensing is reported, both in bare form and coated with few-layer  $\text{MoS}_2$  sheets. Compared to bare aerogel, the  $\text{MoS}_2$ /graphene hybrid aerogel demonstrates selective detection of  $\text{NO}_2$  at ultralow concentrations with fast response and recovery times. The aerogel provides a large surface area, porous structure for gas access, and high electrical conductivity for a low noise measurement. The sensor is realized by integrating the aerogels onto a low-power microheater platform, such that the operating temperature of the sensor can be varied. The detection limit of the  $\text{MoS}_2$ /GA sensor is below 50 ppb  $\text{NO}_2$  at both room temperature ( $\sim 0.1 \text{ mW}$  power consumption) and  $200^\circ\text{C}$  ( $\sim 4 \text{ mW}$  power consumption). At  $200^\circ\text{C}$ , the sensor shows much-improved response and recovery times compared to room temperature, while maintaining low power consumption, thus greatly expanding the practical application of this sensor.

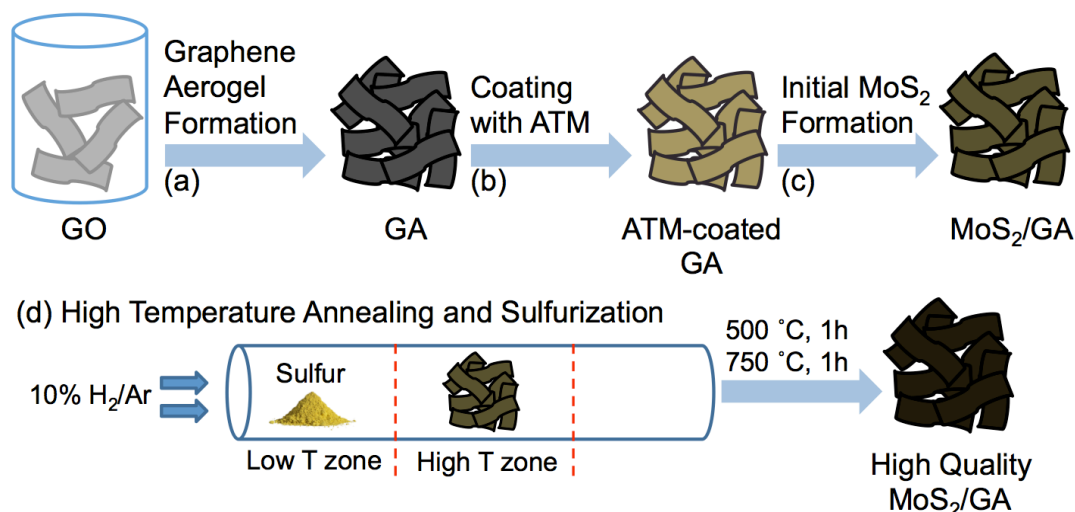
## 2. Material synthesis and characterization

### 2.a. Synthesis of graphene aerogel, $\text{MoS}_2$ aerogel, and $\text{MoS}_2$ /graphene hybrid aerogel

Figure 1 shows a schematic of the  $\text{MoS}_2$ /GA synthesis process, which starts with the graphene aerogel synthesis process (Figure 1a). An electrically conductive, highly crystalline, and

mechanically robust graphene aerogel (GA) with ultra high surface area is prepared according to the method reported in Chapter 4. In a typical process, 3 mL of an aqueous graphene oxide suspension (2 wt% graphene oxide) is mixed with 500  $\mu\text{L}$  concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). The vial is sealed and placed in an oven at 85  $^\circ\text{C}$  for 12 h. The resulting wet gel is washed in deionized water to remove  $\text{NH}_4\text{OH}$ . This is followed by an exchange of water with acetone inside the pores. Supercritical  $\text{CO}_2$  is used to dry the gel that is then converted to the graphene aerogel by pyrolysis at 1050  $^\circ\text{C}$  under nitrogen for 3 hours. The GA undergoes an additional thermal anneal at 2000  $^\circ\text{C}$  in He to improve the graphene crystallinity. The GA has high electrical conductivity ( $112 \text{ S m}^{-1}$ ) [196], high specific surface area ( $1200 \text{ m}^2 \text{ g}^{-1}$ ) [100], and good thermal conductivity. As shown in high resolution TEM images in Ref. [100], the graphene aerogel consists of few-layer graphene sheets connected in a three-dimensional scaffold.

To create the  $\text{MoS}_2$ /graphene hybrid aerogel, the GA is immersed in an aqueous solution of 1  $\text{mol L}^{-1}$  ammonium thiomolybdate (ATM), submerged in liquid nitrogen for rapid freezing and further freeze-drying, and then annealed at 450  $^\circ\text{C}$  under 2%  $\text{H}_2/\text{Ar}$  for 4 h (Figures 1b and 1c) [196]. To further improve the  $\text{MoS}_2$  quality, the aerogel is annealed by a two-step annealing process (Figure 1d). First, the aerogel is placed in the hot zone ( $T_H$ ) of a low-pressure furnace (base pressure of 700 mTorr) while sulfur is placed in the upstream low-temperature ( $T_L$ ) zone of the furnace. With a 10%  $\text{H}_2/\text{Ar}$  mixture flowing continuously through the tube, the aerogel is first heated at  $T_H = 500 \text{ }^\circ\text{C}$  for 1 h to reduce any possible  $\text{MoO}_3$  into  $\text{MoO}_2$ . At this furnace set-point, the low-temperature zone is at  $T_L < 113 \text{ }^\circ\text{C}$ . The furnace is then heated to  $T_H = 750 \text{ }^\circ\text{C}$  for 1 h, at which point the low-temperature zone reaches 120  $^\circ\text{C}$  (above the melting point of sulfur) and sulfur vapor reacts with the aerogel to fully sulfurize the molybdenum. The furnace is cooled back down to room temperature under continued  $\text{H}_2/\text{Ar}$  flow.  $\text{MoS}_2$  aerogel is also synthesized without the graphene aerogel scaffold, for morphology comparison. In this case, 26 mg of ATM is dissolved in 1 mL of de-ionized water in a vial, which is submerged in liquid nitrogen to rapidly freeze the solution. The frozen solution is then freeze-dried and annealed at 450  $^\circ\text{C}$  under 2%  $\text{H}_2/\text{Ar}$  for 4 h to yield the  $\text{MoS}_2$  aerogel.

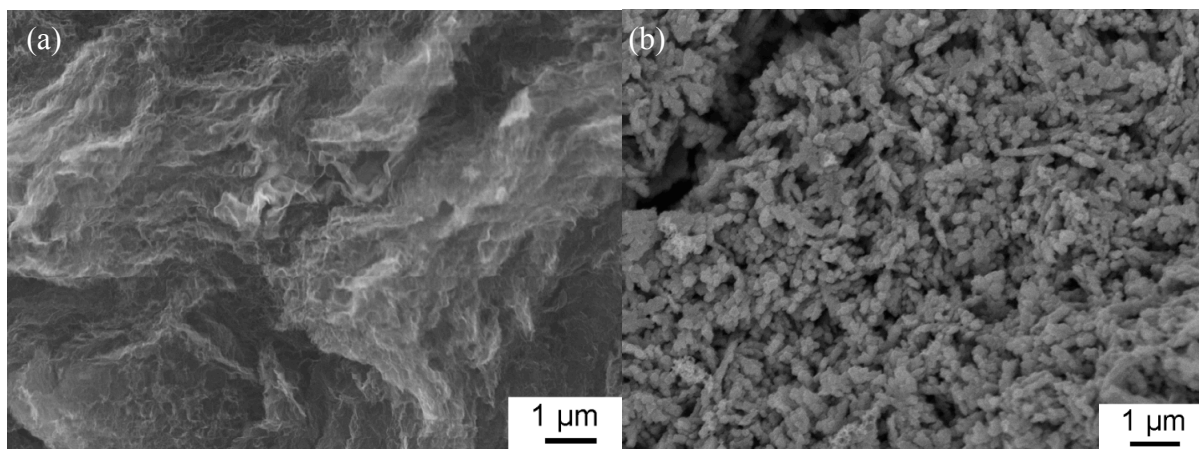


**Figure 1.** Schematic illustration of the synthesis process for MoS<sub>2</sub>/graphene aerogel. (a) Graphene oxide (GO) sheets are cross-linked, supercritically dried, and annealed at high temperature to form graphene aerogel (GA). (b) GA is soaked in a solution of ammonium thiomolybdate (ATM) and freeze-dried. (c) ATM-coated GA is annealed at 450 °C in 2% H<sub>2</sub>/Ar for 4 hours. (d) Two-step high temperature annealing (at 500 °C and 750 °C) for 1 hour each in 10% H<sub>2</sub>/Ar with excess sulfur improves the quality of the final MoS<sub>2</sub>/GA aerogel.

## 2.b. Aerogel characterization

The morphology of the GA, MoS<sub>2</sub>/GA, and MoS<sub>2</sub> aerogel is characterized with scanning electron microscopy (SEM, JEOL JSM-6700F operated at 5 keV with a working distance of 8 mm).

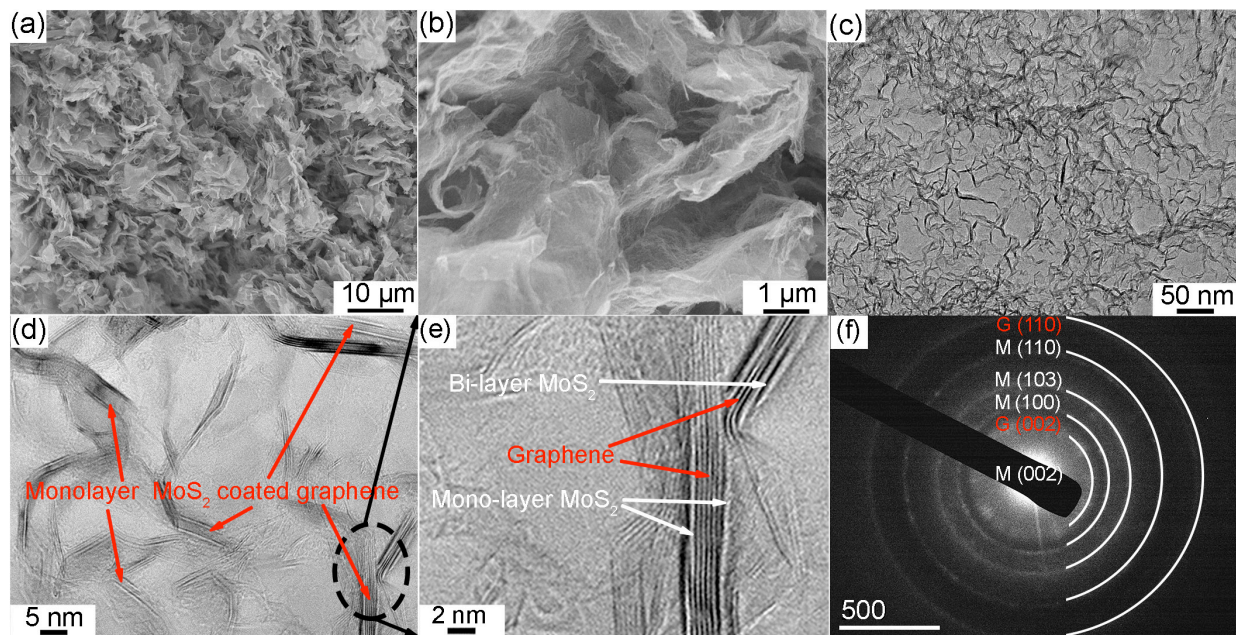
Figure 2a shows the highly porous structure of the graphene aerogel. Analysis of the graphene aerogel specific surface area, pore size, thermal stability, electrical conductivity, and mechanical stability can be found elsewhere [100], [102], [190]. In Figure 2b, the MoS<sub>2</sub> aerogel can be seen to have an aggregated nanoparticle morphology, which explains the low specific surface area that is observed (18 m<sup>2</sup> g<sup>-1</sup>) without the graphene scaffold [196]. SEM images of the as-synthesized MoS<sub>2</sub>/GA (Figure 3a and 3b) show that the hybrid aerogel is in the form of continuous 3D assemblies with thin interconnected sheets. The hybrid aerogel maintains the porous features of the bare GA. The average pore size of the hybrid aerogel is around 6 nm [196]. The open porous network of the MoS<sub>2</sub>/GA allows the aerogel surface area to be readily accessed by improving the gas diffusion.



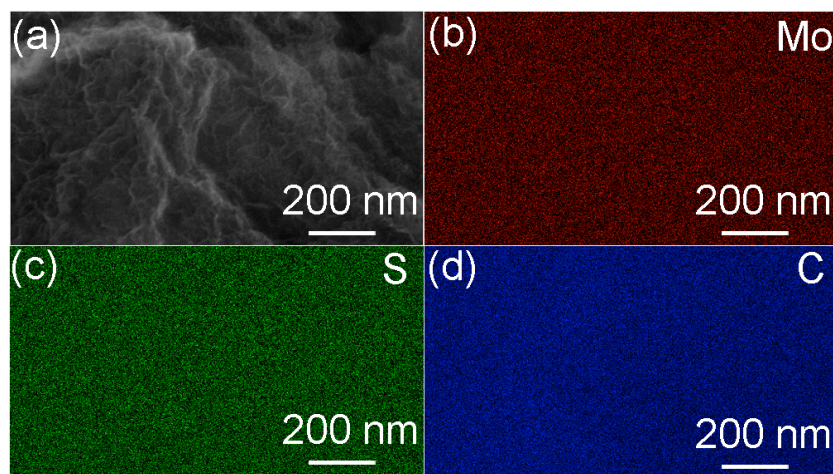
**Figure 2.** (a) SEM image of the bare graphene aerogel. (b) SEM image of the MoS<sub>2</sub> aerogel.

Further analysis of the MoS<sub>2</sub>/GA is done with energy dispersive x-ray spectroscopy (EDX, JEOL 7401-F FESEM), and high-resolution transmission electron microscopy (HRTEM, JEOL 2010 operated at 80 keV). In the HRTEM analysis, shown in Figures 3d-e, the graphene and MoS<sub>2</sub> can be clearly distinguished from their lattice spacings (0.35 nm [206] vs. 0.65 nm [195], respectively). The analysis indicates that most of the graphene scaffold is coated on both sides with MoS<sub>2</sub>, which is present in the form of one to three-layer sheets (mainly monolayer); thus, the benefits of the 2D material are preserved in this 3D structure. The selected-area electron diffraction (SAED) pattern is shown in Figure 3f with several diffraction rings, which can be indexed to the planes of hexagonal-phase MoS<sub>2</sub> (M) and graphene (G) sheets. The uniform distribution of MoS<sub>2</sub> on graphene scaffold is confirmed by energy-dispersive X-ray spectroscopy (EDX) elemental maps shown in Figure 4, where C, Mo, and S are seen to be uniformly distributed throughout the hybrid aerogel. Because the graphene aerogel is conformally coated with single and few-layer MoS<sub>2</sub>, the hybrid structure possesses high specific surface area (700 m<sup>2</sup> g<sup>-1</sup>) [196], an important characteristic for sensing.





**Figure 3.** Morphology of the as-prepared MoS<sub>2</sub>/GA. (a-b) SEM images of the hybrid aerogel with different magnifications. (c) Low magnification TEM image of the MoS<sub>2</sub>/GA. (d) High resolution TEM image of the MoS<sub>2</sub>/GA, showing most of graphene is coated by monolayer MoS<sub>2</sub>. (e) Enlarged TEM image demonstrating the MoS<sub>2</sub> coating of the few-layer graphene scaffold. (f) Relevant selected area electron diffraction (SAED) pattern of the MoS<sub>2</sub>/GA.

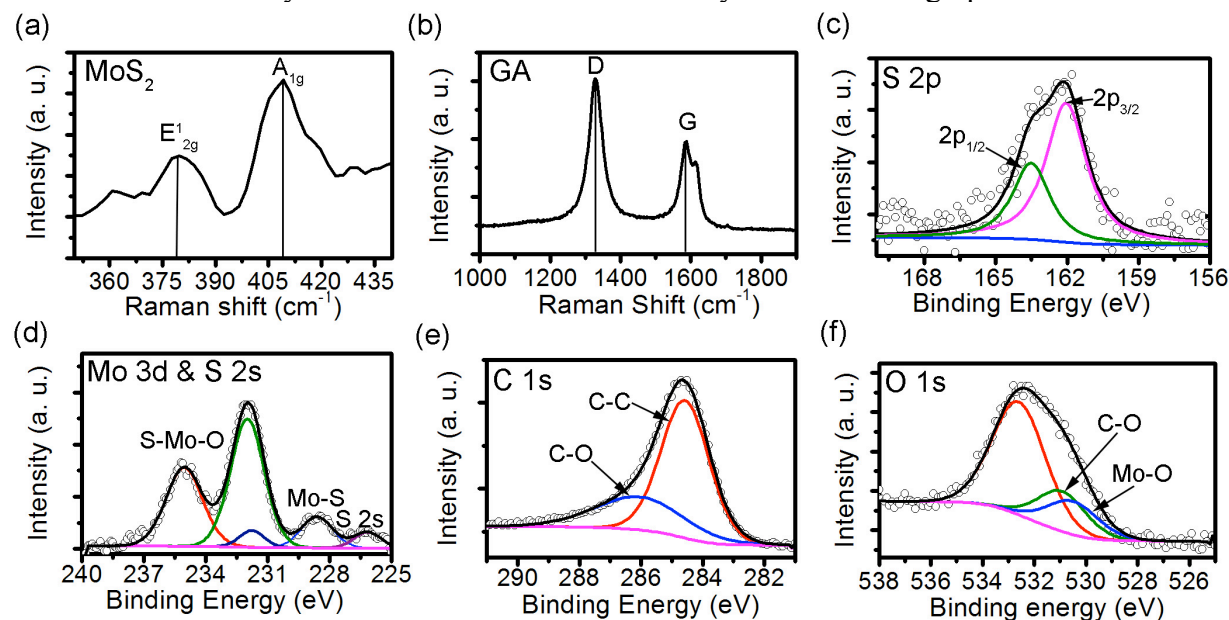


**Figure 4.** (a) SEM image of the hybrid aerogel and the EDX maps of (b) Mo, (c) S, and (d) C showing uniform distribution of all three elements.

To better understand the chemical nature of the MoS<sub>2</sub>/graphene hybrid aerogel, Raman spectroscopy (HORIBA Jobin Yvon LabRam) and X-ray photoelectron spectroscopy (Omicron Dar400 system with an achromatic Al K<sub>α</sub> X-ray source) are used. Raman spectra, shown in Figure 5a and 5b, show the characteristic peaks of MoS<sub>2</sub> and graphene. The major peaks associated with MoS<sub>2</sub> are at 378 and 407 cm<sup>-1</sup> and correspond to the in-plane E<sub>2g</sub><sup>1</sup> and out-of-



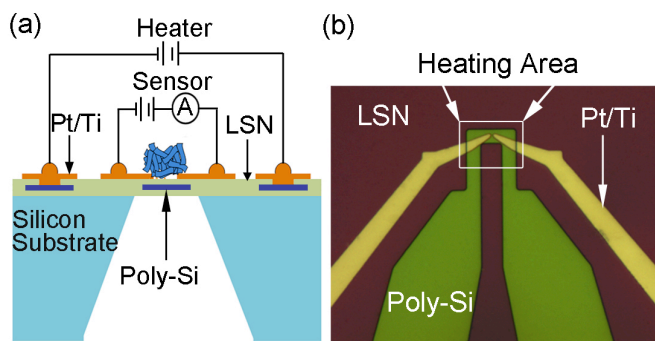
plane  $A_g^1$  vibrational modes of hexagonal  $\text{MoS}_2$ , respectively, in good agreement with literature values for multi-layer  $\text{MoS}_2$ . Two strong peaks observed at  $1357$  and  $1589\text{ cm}^{-1}$  match well with the D and G bands of graphene. X-ray photoelectron spectroscopy (XPS) is used to further study the surface electronic state and composition of  $\text{MoS}_2/\text{GA}$ . Sulfur, molybdenum, carbon and oxygen peaks are clearly identified in the high-resolution scans in Figures 5c-f. The S 2p region shows two characteristic peaks located at  $162.0$  and  $163.1\text{ eV}$  corresponding to S  $2p_{3/2}$  and S  $2p_{1/2}$ , respectively, which can be indexed to Mo-S bonding in  $\text{MoS}_2$ . Surprisingly, the Mo peaks show two Mo oxidation states ( $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$ ), which can be indexed to the Mo-S and the Mo-O bonding, respectively. The calculated S:Mo ( $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$ ) ratio is 2.4, whereas when only the  $\text{Mo}^{4+}$  is used, the S:Mo ratio is 10:1, which suggests it is unlikely that Mo is in a separate molybdenum oxide phase. This is consistent with the absence of molybdenum oxide peaks in Raman spectra. Additionally, the carbon peak (Figure 5e) can be deconvoluted into two peaks, a large peak at  $284.6\text{ eV}$  attributed to C-C bonding environment associated with the graphene scaffold, and a smaller peak at  $286.0\text{ eV}$  attributed to C-O bonding which indicates that Mo-O does not come from a  $\text{MoO}_3$  phase, but rather from a Mo-O-C bonding environment at the interface between  $\text{MoS}_2$  and graphene. The O 1s region (Figure 5f) exhibits three peaks. In addition to the peak at  $532.6\text{ eV}$  that is commonly observed in ex-situ analyzed samples, there is a peak at  $530.5\text{ eV}$  that can be assigned to Mo-O bonding and a peak at  $530.9\text{ eV}$  that can be assigned to C-O bonding, which further corroborates the Mo-O-C bonding. The formation of a Mo-O bond without Mo-S scission has been reported elsewhere [207]–[209], and suggests strong chemical and electronic coupling between the  $\text{MoS}_2$  and graphene in the synthesized aerogel. This unique Mo environment with O- and S-bonding may offer more active defect sites as well as unusual electronic properties [207], [208]. Based on the morphological and compositional characterizations described above, the  $\text{MoS}_2/\text{GA}$  displays a high surface area with a uniform distribution of few-layer  $\text{MoS}_2$  sheets that are covalently bonded to the graphene scaffold.



**Figure 5.** (a-b) Raman spectra of the hybrid aerogel. (c-f) X-ray photoelectron spectra of the  $\text{MoS}_2/\text{graphene}$  hybrid aerogel: (c) S 2p; (d) Mo 3d and S 2s; (e) C 1s; (f) O 1s.

### 3. Sensor Fabrication and Testing

The synthesized aerogels are evaluated for gas sensing by integrating onto a low power microheater platform. Figure 6a shows a cross-sectional schematic of the sensor. The microheater consists of a polycrystalline silicon (Poly-Si) microheater embedded in a low-stress silicon nitride (LSN) membrane with Pt/Ti metal contacts for the microheater and the sensing material. Figure 6b shows a zoomed-in view of a single microheater device showing the two Pt/Ti sensing electrodes (yellow) above the microheater (green) embedded in the LSN membrane (purple). Chapter 2 contains full descriptions of the design and fabrication of the microheater platform. In the previous work using the microheater platform for catalytic gas sensing, the Pt/Ti sensing electrodes are masked with SiO<sub>2</sub> and are not in use. Here, they remain uncovered and the sensing material is deposited on top to bridge the gap and create a circuit that measures the resistance of the sensing material. The gap is positioned directly over the microheater so that the conductance of the heated material is measured. The membrane thermally isolates the heated sensing area and minimizes heat lost through conduction to the silicon substrate. With this design, the heater consumes only 15 mW to reach 700 °C. Besides the low power consumption, the microheater platform has excellent stability in the temperature range of interest and a closed membrane configuration to make sensing material deposition easier. The aerogel is sonicated into suspension in a solution of de-ionized water and isopropyl alcohol and drop-cast onto the microheater while the heater is powered to 3 mW (~100 °C) to drive localized deposition. Care is taken so the aerogel does not connect the sensing electrodes across non-heated parts of the chip.



**Figure 6.** (a) Cross-sectional schematic of the microheater sensor. (b) Optical image of one microheater showing the Pt/Ti sensing electrodes above the polysilicon heater.

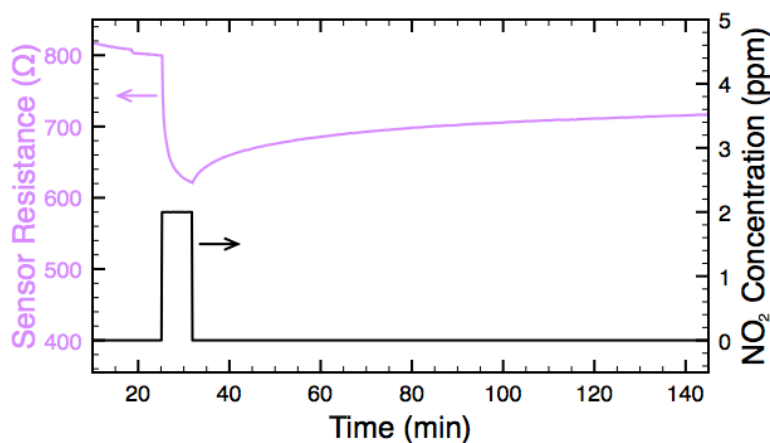
As in previous chapters, the microheater chip is wire-bonded into a 14-pin package for testing within a gas flow chamber with a volume of 1 cm<sup>3</sup>. Nitrogen dioxide (20 ppm in N<sub>2</sub>, Praxair), carbon monoxide (5000 ppm in N<sub>2</sub>, Praxair), and hydrogen (5% in N<sub>2</sub>, Praxair) gas flow is controlled by Bronkhorst mass flow controllers and diluted with clean, dry air for a total flow rate of 300 sccm. Labview is used to control the gas flow. A Keithley 2602A source-meter controlled by Zephyr software is used to power the microheater and obtain the sensor results. A 0.5V bias voltage is applied to the sensing material. The applied voltage on the microheater is changed to give various operating temperatures. The sensor response is determined by the relative change in resistance, which is defined as  $(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}$ , where  $R_{\text{gas}}$  is the resistance during exposure to given gas concentration and  $R_{\text{air}}$  is the average resistance in clean air before any gas exposure.

## 4. Gas Sensing Performance

### 4.a. Graphene aerogel

Single-layer graphene has excellent properties for a sensing material, including the highest possible surface-to-volume ratio and high electrical conductivity [42]. Reduced graphene oxide, which is the basis for our aerogel, has been evaluated for gas sensing purposes [46], [47], including as graphene aerogel composite with metal oxide nanoparticles [210]–[212]. However, the synthesis method of the graphene aerogel can impact the sensing behavior, by imparting varied crystallinity, connectivity, and oxygen content. Therefore, the sensing response of this graphene aerogel has been investigated using a variety of gases known to have strong electronic interaction when adsorbed on graphene. Clean single-layer graphene has a zero bandgap, but graphene can become p- or n-type with particular processing conditions and intentional introduction of dopants. The oxygen-containing groups that remain on graphene synthesized from graphene oxide tend to draw electrons from the carbon sheet, resulting in a p-type material [213]. Therefore, gases that are electron donors will result in a resistance decrease in the graphene, while gases that are electron acceptors will result in a resistance increase.

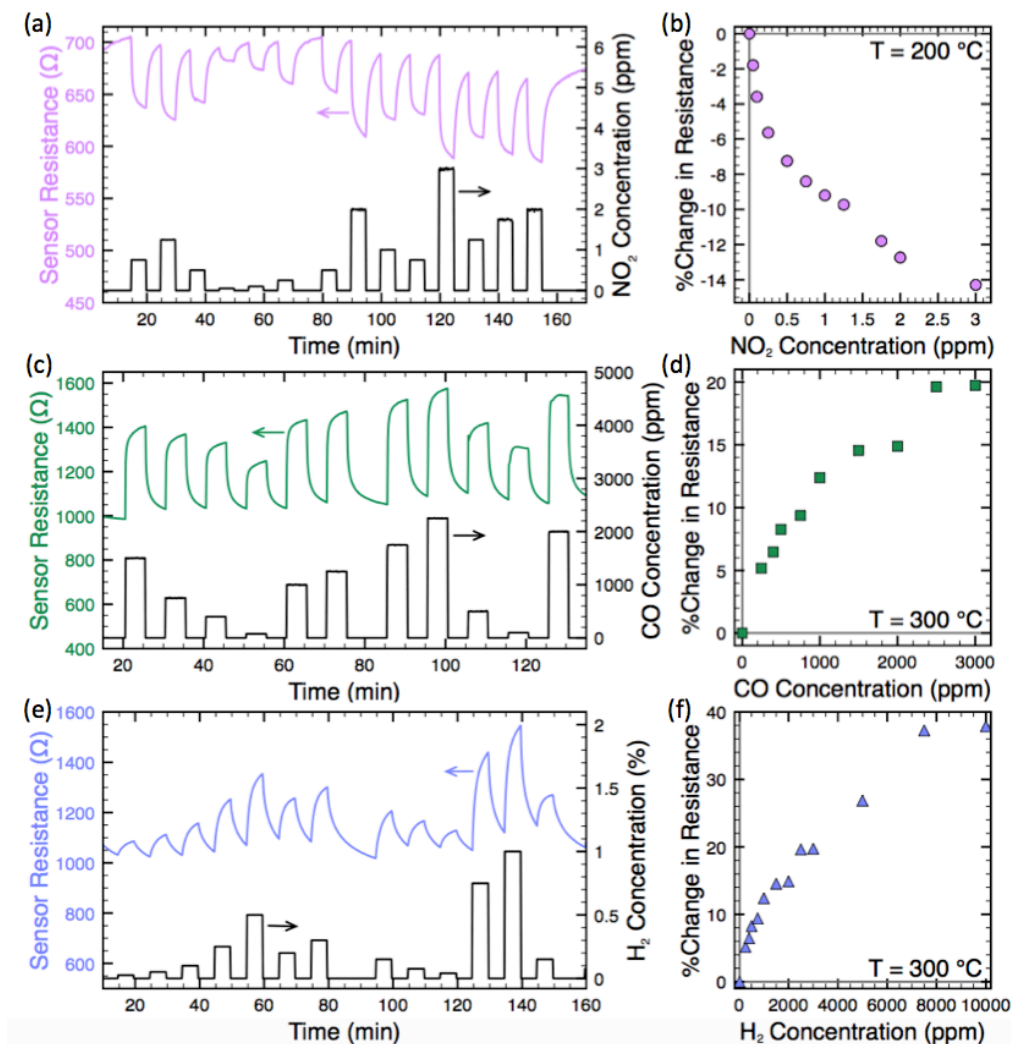
There is much interest in the room temperature operation of graphene-based sensors, but gas desorption is difficult at low temperature and therefore, the sensor cannot fully recover without an input of energy by heating or illuminating with ultraviolet light [42]. In Figure 7, graphene aerogel heated to 100 °C and exposed to 2 ppm NO<sub>2</sub> cannot recover even after 100 minutes in clean air. Therefore, the microheater platform is used to heat the graphene aerogel to 200 or 300 °C, which speeds up the recovery time and the response time. The response time becomes faster because the increased desorption rate also allows for an equilibrium between adsorption and desorption of the gas to be reached more quickly.



**Figure 7.** Graphene aerogel sensor response with an operating temperature of 100 °C showing incomplete recovery after exposure to 2 ppm NO<sub>2</sub>.

Figure 8 details the response of the GA sensor to nitrogen dioxide, carbon monoxide, and hydrogen. The bias voltage applied to the graphene aerogel is 0.5 V. The general trend is as expected for a p-type material, with nitrogen dioxide (an electron donor) resulting in a resistance decrease and CO and hydrogen (electron acceptors) resulting in a resistance increase. Because

nitrogen dioxide is toxic at very low concentrations (53 ppb air quality standard set by the Environmental Protection Agency [191]), a concentration range of 0.05 to 3 ppm is used. Carbon monoxide is also toxic but at higher concentrations (35 ppm air quality standard set by the EPA [192]), so a higher concentration range of 75 to 3000 ppm is tested. Hydrogen gas is not itself toxic but presents dangers due to its flammability and through oxygen displacement. The lower explosive limit of hydrogen is 4% or 40,000 ppm [89], so the tested concentration range is set below that from 250 to 10,000 ppm.



**Figure 8.** (a) GA sensor resistance versus time with exposure to varied NO<sub>2</sub> concentrations. Operating temperature is 200 °C. (b) GA sensor response versus concentration curve for NO<sub>2</sub>. (c) GA sensor resistance versus time with exposure to varied CO concentrations. Operating temperature is 300 °C. (d) GA sensor response versus concentration curve for CO. (e) GA sensor resistance versus time with exposure to varied H<sub>2</sub> concentrations. Operating temperature is 300 °C. (f) GA sensor response versus concentration curve for H<sub>2</sub>.

The response and recovery time at the higher operating temperatures is definitely an improvement over the 100 °C response shown in Figure 7. The  $t_{90}$  response and recovery time, defined as the time to reach 90% of the full signal, is 106 s and 175 s for NO<sub>2</sub> gas, and 85 s and 133 s for CO. Because the hydrogen gas response does not stabilize in the given exposure time, the response and recovery times cannot be calculated. Compared to the catalytic gas sensing response and recovery times, the graphene aerogel sensor is very slow. This is due to the fundamentally different sensing principles, where the catalytic gas sensor starts combusting gas and releasing heat as soon as it arrives at the catalyst, while the graphene sensor conductance changes until an equilibrium is reached between gas adsorption and desorption is reached. These response and recovery times for NO<sub>2</sub> and CO are a strong improvement over previously reported graphene sensors operated at room temperature [47], and are comparable to other heated graphene sensors [46], [52], [214].

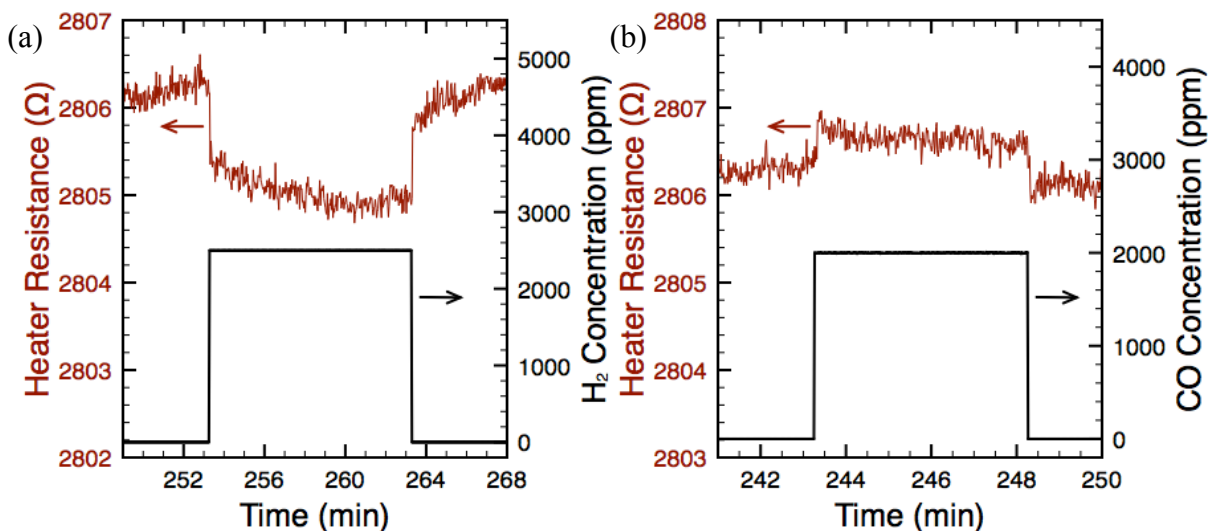
As expected for unfunctionalized graphene, the GA sensor has a strong response to all three gases. To account for the baseline changing a bit due to not quite complete recovery, the sensor response in Figures 8b, d, and f defines the  $R_{\text{air}}$  as the resistance in clean air right before the subsequent gas exposure. The response for all gases seems to plateau at the upper end of the concentration range, indicating that the most of the available gas adsorption sites are occupied and subsequent increases in gas concentration cannot proportionally change the sensor resistance. Hydrogen and carbon monoxide give fairly similar response magnitudes for the same gas concentration. Nitrogen dioxide gives a stronger response given the much lower concentrations used for exposure. The lowest concentration of NO<sub>2</sub> that can be delivered by the testing system is 50 ppb, which gives a response with a signal-to-noise ratio of 12, but using a standard signal-to-noise (S:N) ratio of 3, the lowest detectable concentration should be 12 ppb NO<sub>2</sub>. The calculated limit of detection for S:N ratio of 3 for carbon monoxide is 250 ppb. Although highly sensitive graphene-based sensors for NO<sub>2</sub> have been reported, including single ppb or even single molecule level [42], [214], the magnitude of the graphene aerogel sensor response is similar to other reduced graphene oxide sensors [52], [215].

Selectivity is an important feature for any sensing technology, and given the strong response of graphene to multiple gases, researchers have suggested methods for obtaining more selective measurements from functionalization of the material to multiplexed sensor measurements. Multiplexed sensor measurements typically involve an array of sensor elements, each with a unique response curve for the gases of interest. Often the array includes graphene with various functionalization or decoration, although recent work from Lipatov, et al. demonstrates an array of the same reduced graphene oxide, where the slight variations in deposition create sensor elements with varied response curves [216]. Other strategies have focused on getting more information from one sensor element, through gate variation [217], temperature variation [179], or measurement of the noise frequency spectrum [218]. Given that the GA sensor has two electrical channels, the graphene aerogel conductance and the heater resistance,

As demonstrated in the previous chapters on combustible gas sensing, the microheater is sensitive to changes in temperature. Without a catalytic material, the microheater temperature is still affected by changes in thermal conductivity in the surrounding gas. Because conduction to the air is a major method of dissipating heat generated through Joule heating of the microheater

trace, if the thermal conductivity of the surrounding gas changes, the amount of heat transferred to the gas changes as well. For certain combinations of gases that have very different thermal conductivities, this behavior could be exploited to measure gas concentration. Hydrogen and carbon monoxide are two such gases, where hydrogen has a room-temperature thermal conductivity (TC) of  $0.186 \text{ W m}^{-1} \text{ K}^{-1}$ , carbon monoxide  $0.0232 \text{ W m}^{-1} \text{ K}^{-1}$ , and sea level air  $0.0262 \text{ W m}^{-1} \text{ K}^{-1}$  [219]. If  $\text{H}_2$  is mixed with air, the TC increases, allowing more heat to be dissipated to the air, and therefore decreasing the microheater temperature. The opposite is true for carbon monoxide and the effect is smaller, given the much closer TC values for CO and air.

Hydrogen and carbon monoxide have a problem with cross-sensitivity in a number of sensing methods, including electrochemical [219], [220], catalytic [219], and using bare graphene, as demonstrated here. Electrochemical sensors for carbon monoxide typically have a filter for hydrogen sulfide, which can also give a false signal, but hydrogen can diffuse through and gives a response that is 40-60% of the signal of the equivalent CO gas concentration [220]. Here, the graphene aerogel gives a response of the same magnitude and sign to hydrogen and carbon monoxide at equivalent concentrations (Figure 8d and 8f) with an operating temperature of  $300^\circ\text{C}$ . However, because of the different thermal conductivities, the microheater also responds to the gas presence. As seen in Figure 9, the microheater response has different signs and magnitudes for the two gases, with the hydrogen leading to a larger negative change where the CO has a small positive change. The response is additionally much faster than the graphene aerogel conductance. The microheater response magnitude does depend on the gas concentration but the sensitivity is much lower than the graphene aerogel. If the microheater channel is monitored in addition to the graphene sensor channel, then the gas can be identified on one channel and quantified on the other.



**Figure 9.** (a) Heater response during 2500 ppm hydrogen exposure with  $300^\circ\text{C}$  operating temperature. (b) Heater response during 2000 ppm CO exposure with  $300^\circ\text{C}$  operating temperature.



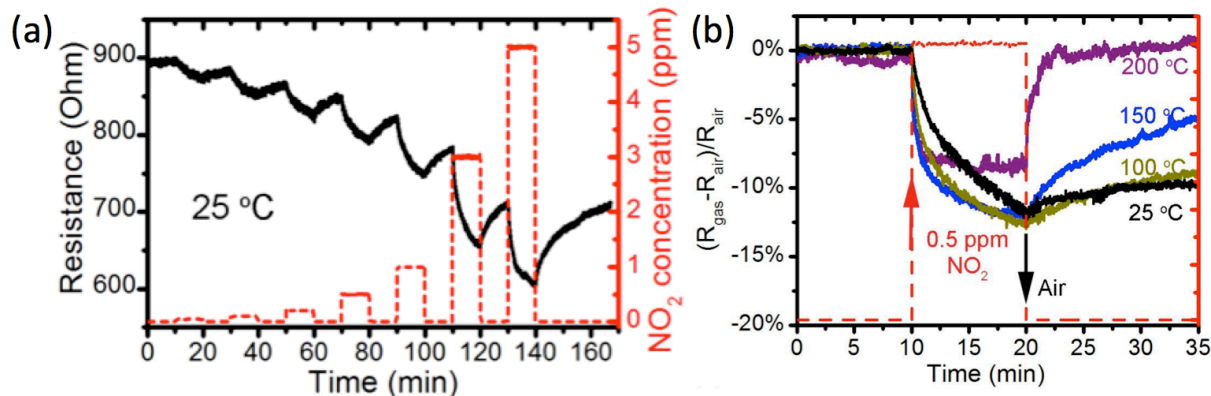
While using the microheater as a secondary information source can allow for additional selectivity, it makes the measurement more computationally intensive. Coating the graphene aerogel to lend intrinsic selectivity to the sensing material is also explored as a technique for improving the selective performance of the sensor.

#### 4.b MoS<sub>2</sub>/graphene hybrid aerogel

The hybrid MoS<sub>2</sub>/graphene aerogel, which consists of single- to few-layer MoS<sub>2</sub> sheets coating the graphene aerogel, maintains high conductivity and high specific surface area (especially compared to MoS<sub>2</sub> aerogel alone). Coating the aerogel with 2D sheets rather than loading with nanoparticles increases the contact area for efficient charge transfer from the MoS<sub>2</sub> to the graphene and vice versa. The Mo-O-C bonding observed with XPS indicates tight chemical and electronic coupling and the excess sulfur may offer more active defect sites for strong gas adsorption.

After deposition on the microheater platform, the MoS<sub>2</sub>/GA sensor exhibits a linear current-voltage response. Figure 10a shows a typical gas sensor response curve at room temperature towards different NO<sub>2</sub> concentrations, from 50 ppb to 5 ppm, at a bias voltage of 0.5 V. Upon exposure to NO<sub>2</sub>, the sensor resistance exhibits a pronounced decrease. The sensing mechanism relies on the direct charge transfer between NO<sub>2</sub> and MoS<sub>2</sub>/GA. Nitrogen dioxide is a known electron acceptor due to the unpaired electron on the nitrogen atom, so the decrease in resistance upon NO<sub>2</sub> adsorption indicates p-type behavior from the hybrid aerogel. Since the bare graphene aerogel shows the same p-type behavior, it is clear that the MoS<sub>2</sub> coating does not change the semiconductor behavior. During subsequent exposure to clean air, the sensor resistance very slowly recovers as NO<sub>2</sub> molecules desorb from the surface. This behavior is consistent with the charge transfer mechanism of single-layer graphene [43], MoS<sub>2</sub> [50], and carbon nanotube gas sensors [221]. As reported for reduced graphene oxide and few-layer MoS<sub>2</sub> sensors, the adsorption of gas can be divided into two components, adsorption on low energy binding sites (such as sp<sup>2</sup> bonded carbon) and on high energy binding sites (defects including vacancies and functional groups) [48]. The low energy binding sites induce a rapid response through weak dispersive forces, while the high energy sites allow slow but strong binding [222]. As seen in Figure 10a, the slow rates of response and recovery at room temperature suggest defect-dominated adsorption. The S-Mo-O bonds and the excess sulfur, based on the XPS analysis, may be the source of these defects. The defect sites explain the high sensitivity even for very low concentrations of gas. In Figure 10a, a clear response is visible even at a NO<sub>2</sub> concentration of 50 ppb (the lowest concentration that can be accurately delivered by the gas delivery system), which is lower than most single- or few-layer MoS<sub>2</sub> transistor-based sensors (Table 1). Given the size of the response to 50 ppb, it is expected that the sensor would respond to even lower concentrations of NO<sub>2</sub>.





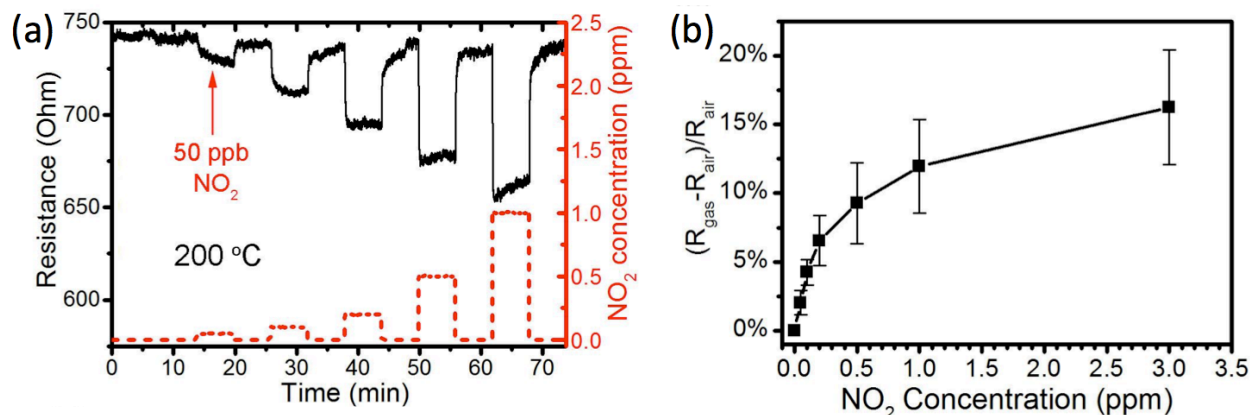
**Figure 10.** (a) Real time response of the sensor at room temperature towards different NO<sub>2</sub> concentrations. (b) Sensor response to 0.5 ppm NO<sub>2</sub> at various microheater temperatures, displaying improvement in response and recovery time.

At room temperature, the response and recovery rates are slow, because of the strong adsorption of NO<sub>2</sub> on MoS<sub>2</sub> surface, which is also observed in carbon nanotube [221], [222], graphene [194], [223], and MoS<sub>2</sub> [50], [53], [187] sensors. Incomplete recovery of the sensor leads to an unreliable sensing output in practical applications. Heating the sensing material with a microfabricated heater can enhance the reversibility of the sensor and accelerate the response and recovery rates, while maintaining low power consumption [97], [110], [178], [189]. Figure 10b shows the sensor response to 0.5 ppm NO<sub>2</sub> at various heating temperatures, ranging from room temperature to 200 °C. At 200 °C (with the microheater consuming ~4 mW), the sensor shows fast response and complete recovery. The magnitude of the sensor response to NO<sub>2</sub> is, however, slightly smaller at high temperature than at low temperature. This behavior is consistent with the proposed sensing mechanism. At low temperature, the adsorption of NO<sub>2</sub> is substantial and continues during the gas exposure, while desorption is negligible due to the strong bonding between NO<sub>2</sub> and MoS<sub>2</sub>/GA. An equilibrium between adsorption and desorption is not reached within a practical timeframe and the sensor resistance decreases as NO<sub>2</sub> coverage continues to increase. The NO<sub>2</sub> desorption is enhanced at higher temperature, which speeds up the time to reach a balance between adsorption and desorption during gas exposure and during recovery. Although the response and recovery times might be even faster at higher temperature, 200 °C provides an effective temperature when also considering the sensor power consumption.

**Table 1.** Sensing performance of MoS<sub>2</sub> and graphene sensors to gases as reported in the literature and the present work

| Materials                              | Sensing Temperature [°C] | Response Time [s] | Recovery Time [s] | NO <sub>2</sub> Detection Limit [ppb] |
|----------------------------------------|--------------------------|-------------------|-------------------|---------------------------------------|
| Single layer graphene [223]            | 250                      | 26                | 480               | 500                                   |
| 2 nm MoS <sub>2</sub> film [49]        | 25                       | 3600              | 3600              | 500                                   |
| 5-layer MoS <sub>2</sub> [53]          | 25                       | 250               | 500               | 100,000                               |
| Atomically thin MoS <sub>2</sub> [187] | 25, 100                  | —                 | —                 | 1500                                  |
| Atomically thin MoS <sub>2</sub> [186] | 25                       | —                 | —                 | 120                                   |
| Single-layer MoS <sub>2</sub> [54]     | 200                      | 660               | 720               | 20                                    |
| 3D graphene foam [224]                 | 130                      | 300               | —                 | 20,000                                |
| This work – GA                         | 200                      | 106               | 175               | 12                                    |
| This work – MoS <sub>2</sub> /GA       | 200                      | 22                | 29                | 14                                    |

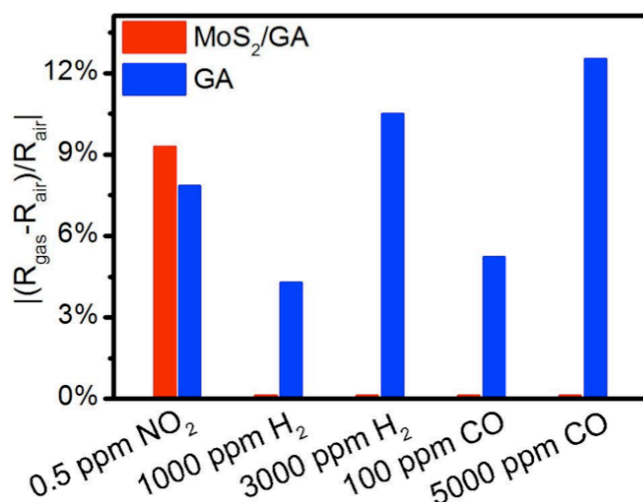
The sensor is further tested at 200 °C against different NO<sub>2</sub> concentrations, from 50 ppb to 1 ppm. As shown in Figure 11a, the sensor shows increased response at higher NO<sub>2</sub> concentrations. Response and recovery times for all NO<sub>2</sub> concentrations are fast. The average time to reach 90% of the stable sensor signal ( $t_{90}$ ) is 22 s for response and 29 s for recovery, which is even faster than the bare graphene aerogel. The reason for this is unclear but may be due to the increased number of defect sites in the MoS<sub>2</sub>/GA compared to bare GA, which result in a greater degree of charge transfer upon gas adsorption [55] such that the resistance changes more significantly in the first minute of exposure. The sensor shows clear response to 50 ppb NO<sub>2</sub> with fast response and nearly complete recovery and a signal to noise ratio of about 11. By using a signal to noise threshold of 3, the calculated detection limit of the sensor is 14 ppb NO<sub>2</sub>. Compared to other graphene- and MoS<sub>2</sub>-based NO<sub>2</sub> sensors listed in Table 1, the sensor presented shows superior sensing performance such as low detection limit and fast response and recovery.



**Figure 11.** (a) Real-time resistance change of the sensor with the microheater temperature of 200 °C. (c) Absolute magnitude of the response versus NO<sub>2</sub> concentration for microheater temperature of 200 °C.

Figure 11b is a plot of sensor response versus NO<sub>2</sub> concentrations, displaying a nonlinear relationship between the gas concentration and the sensor response. Assuming the gas adsorption is dominated by high-energy defect sites, at low NO<sub>2</sub> concentrations when most of the sites are available, the degree of charge transfer is directly proportional to the gas concentration. At higher NO<sub>2</sub> concentrations, the sites may eventually all be occupied during the gas exposure, and thus the response reaches a saturation point. The response level is similar to that of bare graphene aerogel in terms of the magnitude.

In order to better assess the benefit of the MoS<sub>2</sub> coating, the NO<sub>2</sub> sensing performance with pure graphene aerogel was probed. As seen in Figure 12, the GA sensor has similar NO<sub>2</sub> sensing response as the MoS<sub>2</sub>/GA, but the selectivity is much improved with the addition of MoS<sub>2</sub>. The MoS<sub>2</sub>/GA sensors are exposed to high concentrations of carbon monoxide (CO) and hydrogen (H<sub>2</sub>) to compare with the bare GA sensor. While the GA responds to all of the tested gases, the MoS<sub>2</sub>/GA only responds to NO<sub>2</sub>, even though the concentration is much lower. Previous theoretical study shows that NO<sub>2</sub> possesses the largest binding energy compared to CO and H<sub>2</sub> when adsorbed on MoS<sub>2</sub> [225]. This is likely the reason why the MoS<sub>2</sub>/GA hybrid has good selectivity against CO and H<sub>2</sub>. In addition, the extra S in the structure may provide improved selectivity due to the possibility for increased number of bridging S atoms at the edges of MoS<sub>2</sub> [226]. Further study is needed to more fully understand the mechanism behind the selectivity reported here.



**Figure 12.** Selectivity of the MoS<sub>2</sub>/GA sensor compared to GA alone for microheater temperature of 200 °C.

## 5. Conclusion

In summary, the high specific surface area graphene aerogel that has been effectively used with catalytic nanoparticle loading for combustible gas sensing can also be used as a sensing material in a conductometric sensing device configuration. The high quality graphene aerogel has high specific surface area, porosity, and high electrical and thermal conductivity, all of which make it useful as a sensing material. Bare graphene aerogel gives high response to nitrogen dioxide, hydrogen, and carbon monoxide when heated with the microheater platform. The response and recovery times (~1-3 minutes) are much longer than the combustible gas sensing but comparable to other reported works. The selectivity of the graphene aerogel can be improved for hydrogen and carbon monoxide by also taking into account the change in the microheater resistance, as the heater temperature changes with the thermal conductivity of the surrounding gas.

To improve the sensing performance further, a MoS<sub>2</sub>-coated graphene hybrid aerogel is synthesized and characterized. The graphene aerogel is covered with single to few-layer MoS<sub>2</sub> sheets, which provide the sensitive and selective sensing performance. The hybrid aerogel is integrated onto a low-power microheater platform for NO<sub>2</sub> sensing evaluation. The sensor exhibits an ultralow detection limit of 50 ppb NO<sub>2</sub> at both room temperature and 200 °C. By heating the material to 200 °C, a fast response and recovery of the sensor (<1 min) is achieved, which greatly expands the practical application of the sensor. The MoS<sub>2</sub>/GA shows good selectivity against H<sub>2</sub> and CO, especially when compared to bare GA. The improved detection limit, sensitivity, and selectivity can be attributed to the unique structure of the hybrid aerogel. The bonding between the MoS<sub>2</sub> and graphene results in strong electronic coupling and the excess sulfur creates defects that improve the sensitivity of the sensor. The MoS<sub>2</sub>/GA aerogel leverages the properties of the two materials to result in a high performance hybrid material for ultra-sensitive and fast NO<sub>2</sub> sensing and suggests the possibility of other 2D material combinations for sensing applications with improved selectivity.

## Chapter 8. Localized Growth of Porous Metal Oxide Sensing Film on Microheater Platform<sup>7</sup>

### 1. Motivation

Solid-state chemical sensors have received considerable attention in recent years, in particular for monitoring environmental pollution and air quality [227]–[231]. Semiconducting metal oxide sensors are among the most promising solid-state chemical sensors due to the large variety of metal oxides available and their low cost in mass production [230]–[232]. However, in order to obtain appropriate sensitivity levels, the metal oxides need to be heated to high temperature ( $\sim 300$ – $500$  °C), resulting in high power consumption (typically several hundred mW) and thus impeding their implementation as long-term, battery-powered gas monitors [232]–[234]. Power consumption can be decreased by reducing the sensor size and/or the operational sensing temperature. Metal oxide gas sensor miniaturization can be accomplished through the use of microfabrication methods to create a microheater platform [79], [97], [110], [235], [236]. Microheaters allow for high sensing temperatures to be reached with low input power through the use of a small heating element thermally isolated from the substrate. However, the shrunken device footprint means a loss of area for the sensing material, which negatively impacts sensitivity and lifetime. Nanostructured materials with high surface-to-volume ratios can improve the sensitivity through an increase in surface area per device footprint as well as a greater number of grain contacts in the conductive path, which amplifies the signal during gas exposure [233].

Nanostructured metal oxides have been shown to have better gas sensing performance than the corresponding bulk material [233]. However, the integration of networks of nanowires or nanoparticles onto a microfabricated platform is difficult to control. Nanomaterial aggregation during film formation and sensor operation leads to a loss of active surface area and slows the diffusion of the target gas to the active sites [237], [238]. Formation of nanostructured films through the use of sacrificial templates such as polystyrene spheres [237], [238], carbon nanotubes [239], [240], or anodized aluminum oxides [241] adds complexity and cost. There remains a need for a simple, effective approach to the preparation of nanostructured metal oxide films for low power, miniaturized gas sensors.

We have developed a strategy for the fabrication of high performance, miniaturized gas sensors through on-chip generation of highly porous and nanostructured metal oxide films. Tin oxide, the most widely investigated metal oxide sensor material, is taken as the example to demonstrate the validity of this strategy. Taking advantage of the fast thermal response of the microheater platform, a liquid precursor is drop-casted onto the microheater and rapidly sintered to form a porous film of SnO<sub>2</sub> nanoparticles, which yields high surface area and allows for fast gas diffusion to all active sites. The exceptional gas sensing performance of the nanostructured SnO<sub>2</sub>

---

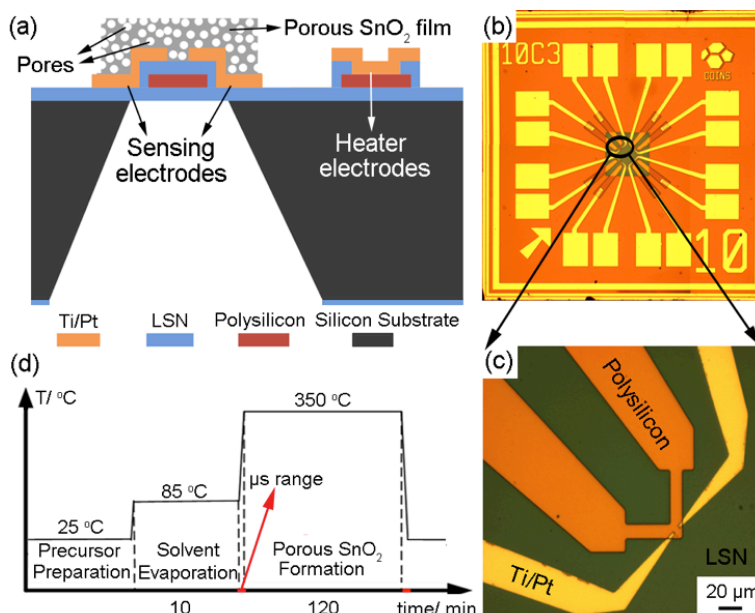
<sup>7</sup> Reproduced with permission from [H. Long, A. Harley-Trochimczyk, T. He, T. Pham, Z. Tang, T. Shi, A. Zettl, W. Mickelson, C. Carraro, R. Maboudian. “In situ localized growth of porous tin oxide films on low power microheater platform for low temperature CO detection,” ACS Sensors, vol. 1, pp. 339–343, 2016.] Copyright [2016] American Chemical Society.

film is demonstrated with fast, highly sensitive response to carbon monoxide at low operating temperature.

## 2. Material synthesis and characterization

The microsensor consists of a porous nanostructured  $\text{SnO}_2$  layer contacted by platinum electrodes deposited on a polycrystalline silicon (polysilicon) microheater embedded in a thin low-stress silicon nitride (LSN) membrane as illustrated in the cross-sectional schematic in Figure 1a. Figure 1b shows a real color optical image of the  $3.5 \times 3.5 \text{ mm}^2$  chip containing four microheater sensors. Full fabrication details can be found in Chapter 2. The microheaters used in this work are  $10 \text{ }\mu\text{m}$  wide,  $100 \text{ nm}$  long, and  $100 \text{ nm}$  thick. No particular surface treatment is done to the chip before the metal oxide coating, except a basic cleaning to remove the photoresist used to protect the wafer surface during dicing (rinsed with acetone, isopropyl alcohol (IPA), de-ionized water, and dried with nitrogen). Figure 1c shows a zoomed-in view of a single microheater device with a heated area of only  $50 \times 50 \text{ }\mu\text{m}^2$ , which results in a low power consumption ( $\sim 18 \text{ mW}$  to reach  $500 \text{ }^\circ\text{C}$ ). The sensing electrodes have a gap of only a few  $\mu\text{m}$  over the hottest region of the microheater, such that the sensor resistance is dominated by the metal oxide at this precise spot. Besides the low power consumption, other benefits of the microheater platform include the fast thermal response time ( $< 100 \text{ }\mu\text{s}$ ) [79], and excellent stability in the temperature range of interest ( $200\text{--}450 \text{ }^\circ\text{C}$ ) [79], [110]. Additionally, the closed membrane configuration makes deposition of sensing material from a liquid precursor much easier compared to bridge microheater structures.

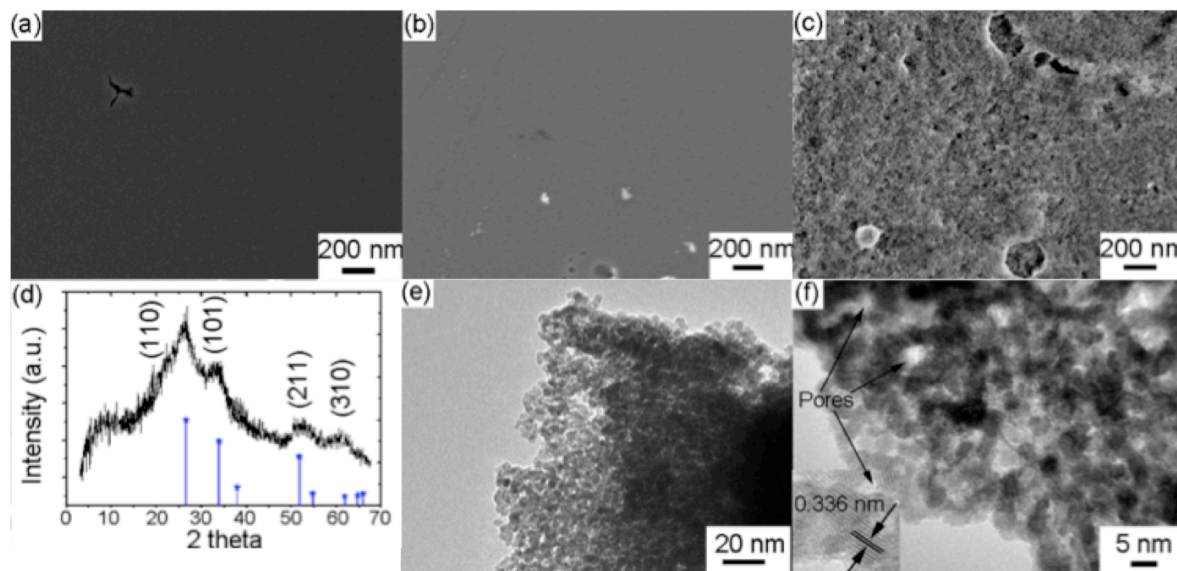
The liquid  $\text{SnO}_2$  precursor is prepared by mixing  $\text{SnCl}_4$ ,  $\text{NH}_4\text{OH}$ , ethanol, and water under continuous stirring at room temperature. After stirring for 1 hour, a  $1 \text{ }\mu\text{L}$  drop is placed on the packaged microheater chip and the heater is powered to  $85 \text{ }^\circ\text{C}$  for 10 min to evaporate the solvent. The addition of  $\text{NH}_4\text{OH}$  in the mixture helps form a gel-like phase [242], [243], that leads to a relatively smooth, uniform precursor film upon deposition and solvent evaporation, as seen in the scanning electron microscopy, SEM (JEOL JSM-6700F) image in Figure 2a. After the 10 min heating at  $85 \text{ }^\circ\text{C}$ , the microheater temperature is ramped to  $350 \text{ }^\circ\text{C}$  ( $12.5 \text{ mW}$ ) and held there for 2 hours to form the final porous  $\text{SnO}_2$  film. Because of the fast thermal response time of the microheater, the temperature reaches  $350 \text{ }^\circ\text{C}$  in less than 1 ms, which leads to the quick removal of water from the gel-like precursor film to form a highly porous  $\text{SnO}_2$  film. As widely explored in the fabrication of activated carbons, a fast heating rate leads to the formation of mesopores or macropores in the structure because of the rapid release of gaseous products [244]–[246].



**Figure 1.** (a) Schematic of the low power microheater-based sensor design. (b) Optical image of a four-element microheater chip with size of 3.5 x 3.5 mm. (c) Enlarged optical image of one microheater, where the deep green color indicates LSN membrane, the orange color indicates polysilicon heater, and the yellow color indicates Pt sensing leads. (d) Temperature profile used for *in-situ* synthesis of the porous  $\text{SnO}_2$  sensor.

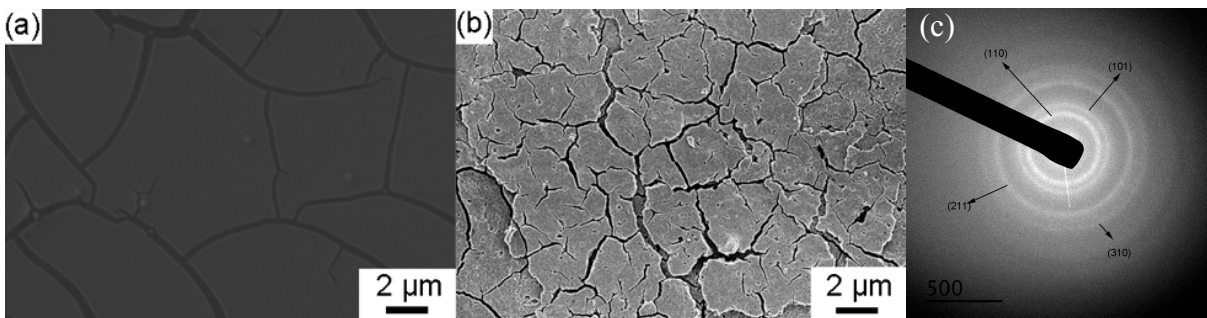
To understand the effect of heating rate, samples are prepared on silicon chips using an external hotplate. In the fast ramping case, the hotplate is preheated to 350 °C and the sample is placed on it after the 85 °C treatment. In the slow ramping case, the sample remains on the 85 °C hotplate and the temperature is changed to 350 °C, which is reached after several minutes. The film is annealed for two hours after the hotplate reaches the set temperature. The thickness of the film is measured with a KLA Tencor Alpha-Step IQ Profiler and yields an average thickness of 350 nm. In Figure 2b, the film produced under slow heating rate is very smooth, comparable to the precursor film in Figure 2a. On the other hand, SEM images of the  $\text{SnO}_2$  film made with the fast heating rate show more cracks and higher surface roughness than the precursor film and the slow heating rate film, confirming that the fast heating rate is the key to the porosity of the film. Increased film porosity in the sintered  $\text{SnO}_2$  film is seen at several length scales from micron-sized cracks (Figure 3) to nanometer-sized pores (Figure 2e). The high-resolution SEM images were taken with JEOL Zeiss Gemini Ultra-55. The composition and phase purity of the sintered film are examined by X-ray diffraction (XRD, Bruker AXS D8 Discover GADDS), with a Vantec-500 area detector, operated at 35 kV at a wavelength of  $\text{Co}, K\alpha, 1.79\text{\AA}$ . All observable diffraction peaks of the film in Figure 2d can be indexed to the tetragonal rutile  $\text{SnO}_2$  structure (JCPDS 41-1445), which confirms the conversion of the precursor to polycrystalline  $\text{SnO}_2$ .





**Figure 2.** SEM images of (a) smooth  $\text{SnO}_2$  precursor film, (b)  $\text{SnO}_2$  film formed with slow heating rate, and (c)  $\text{SnO}_2$  film formed with fast heating rate. (d) XRD data confirming tetragonal rutile  $\text{SnO}_2$  structure for film found in (c). (e) Low and (f) high magnification TEM images of porous  $\text{SnO}_2$  film with small size interconnected nanoparticles. Inset: high resolution TEM indicating the lattice spacing of 0.336 nm, corresponding to (110) crystal structure of  $\text{SnO}_2$ .

The nanoscale features of the porous  $\text{SnO}_2$  film are visible using transmission electron microscopy (TEM). In Figures 2e and f, interconnected nanoparticles with an average size of 4 nm are shown. Smaller particles have higher surface to volume ratios, which are favorable for gas sensing applications due to both the increased number of active sites per device footprint as well as the increased number of grain contacts in the conductive sensing path [247]–[249]. Numerous inter-particle pores with diameters of 1–4 nm are uniformly distributed throughout the film. The inset of Figure 2f shows a lattice spacing of 0.336 nm, which can be readily indexed to the (110) crystal plane of the  $\text{SnO}_2$ , further confirming the formation of crystalline  $\text{SnO}_2$ . The corresponding selected area electron diffraction (SAED) pattern shown in Figure 3c also indicates the polycrystalline nature of the  $\text{SnO}_2$ . The SAED diffraction rings, plus the high background and broad XRD peaks confirm the TEM observation of nanosized  $\text{SnO}_2$  particles.



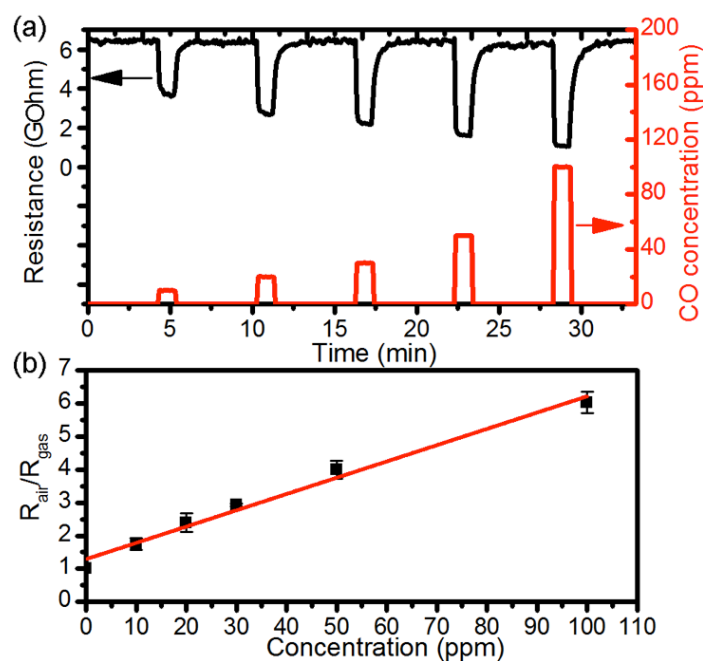
**Figure 3.** Low-magnification SEM image of (a) the SnO<sub>2</sub> precursor film after evaporating the solvent at 80 °C and (b) the porous SnO<sub>2</sub> film, showing a greater number of microscale cracks in the film after the sintering at 350 °C for 2 hours. (c) Corresponding SAED pattern of the porous SnO<sub>2</sub>. The diffraction rings are respectively assigned to the (110), (101), (211), (310) planes.

The porosity of the SnO<sub>2</sub> film on multiple length scales is expected to enhance gas sensing performance because it offers channels for gas diffusion to a large number of active sites [237], [248], [250]. The porous features of the film are defined through the fast heating rate supplied by the microheater, making this a simple method to integrate a porous nanostructured sensing film onto a microheater-based sensor. Because the precursor solution is liquid, it is possible to manufacture these sensors with materials printing methods without concerns about stable suspensions of nanomaterials or clogged printer heads. Additionally, there is no concern about obtaining a connected network of nanomaterials between the sensing electrodes, as the liquid precursor is converted to the nanostructured metal oxide film precisely where required.

### 3. Low-temperature CO detection

To demonstrate that the as-fabricated porous SnO<sub>2</sub> film is directly useful as a gas sensor, the detection of carbon monoxide is explored. The microheater CerDIP package is placed within a gas flow chamber with a volume of 1 cm<sup>3</sup>. The sensor was exposed to CO using a computer-controlled gas delivery system. A cylinder of 5000 ppm CO gas balanced in nitrogen was used (Praxair). Sensor testing is performed at a constant flow rate of 300 SCCM. Stream balance and purge are made up of house air that has passed through pressure swing adsorption dryers to remove humidity and an activated carbon scrubber to remove other contaminants. Mass flow controllers (Bronkhorst) controlled by LabView are used to dilute the gas mixture cylinder with clean air and deliver these gases to the sensor chamber. Flow stream temperatures are within a few degrees of room temperature. The measurement of the microheater sensor is performed using a Keithley 2602A dual-channel source-meter. The source-meter is controlled using Zephyr, an open-source Java-based instrument and control and measurement software suite. A bias voltage of 0.5 V is applied to the sensor channel to measure the resistance of sensor channel. A variable power (controlled by voltage) is applied to the microheater to control the operation temperature. All the information from the source-meter, the gas delivery system, such as flow rates and concentrations, and any reference sensors, such as temperature sensors, is also recorded by Zephyr. The current through the sensor channel is also recorded and its resistance,  $R$ , is calculated. The sensor response is determined by the relative change in resistance, which is defined as  $R_{\text{air}}/R_{\text{gas}}$ , where  $R_{\text{air}}$  is the average sensor resistance in clean air and  $R_{\text{gas}}$  is the average sensor resistance during CO exposure once the response has stabilized.

Figure 4a shows real time resistance change of the SnO<sub>2</sub> sensor to various CO concentrations with a microheater operating temperature of 200 °C, which requires only 7 mW power consumption for continuous measurement. As seen in Figure 4a, the sensor resistance shows rapid response during exposure to varied CO concentrations and full baseline recovery. Tin oxide is an n-type semiconductor and its resistance is determined by surface states, which are affected by the adsorption of oxygen species [35], [36]. In ambient air, chemisorbed oxygen species on SnO<sub>2</sub> surface trap electrons, creating an electron-depleted region, which leads to a barrier at the interface between contacting nanoparticles [35], [36], [239], [251]. The introduction of CO onto the surface at elevated temperatures leads to reaction of CO with the surface oxygen species to form CO<sub>2</sub>. The removal of the oxygen releases the trapped electrons and lowers the barrier between contacting nanoparticles, which leads to a decrease in resistance. Figure 4(b) is a plot of the sensor response ( $R_{\text{air}}/R_{\text{gas}}$ ) versus CO concentration, exhibiting a linear relationship, where  $R_{\text{air}}$  is the average sensor resistance in clean air and  $R_{\text{gas}}$  is the average sensor resistance during CO exposure once the response has stabilized. The sensitivity is comparable to earlier published work [236], [241], [247], [251], [252], but with a lower operating temperature (200 °C vs. 300-500 °C), which allows for lower power consumption. The responses of three devices are within 20% of one another on average, demonstrating the uniformity of this process. Due to the accuracy of the mass flow controllers in the gas delivery system, the lowest CO concentration that can be reliably delivered is 10 ppm (corresponding to signal-to-noise threshold of 17.4), but using a typical signal-to-noise threshold of 3, the detection limit of the sensor is 1.75 ppm.

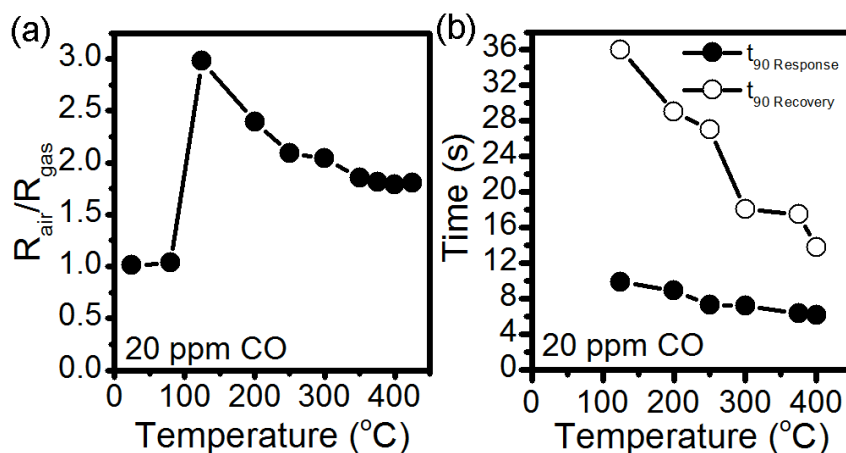


**Figure 4.** (a) Real time resistance change of the sensor for varying CO concentration versus time at 200 °C (7 mW). (b) Sensor response ( $S = R_{\text{air}}/R_{\text{gas}}$ ) to different CO concentration at 200 °C.

The reported operating temperature of 200 °C is an optimum value when considering the sensitivity, the response and recovery time, and the power consumption. As seen in Figure 5, the response to 20 ppm CO is the highest at 125 °C, and decreases with higher temperature to

eventually plateau at 1.8 and the response and recovery time continuously decrease with increasing temperature. Operation at 200 °C gives a recovery time <30 s, sensitivity above 2 for 20 ppm, and power consumption of ~7 mW.

The enhancement in gas-sensing properties of the porous SnO<sub>2</sub> sensor may be ascribed to the small crystalline size of the interconnected nanoparticles, which gives a high surface to volume ratio and generates more active sites per device footprint [240]. Additionally, the small crystal size increases the number of grain contacts in the conductive path between sensing electrodes, increasing the number of energy barriers that are the main source of sensitivity [240], [253]–[256]. The average time to reach 90% of the stable sensor signal ( $t_{90}$ ) is 9 s and the  $t_{90}$  for recovery is 29 s. Other reported SnO<sub>2</sub>-based sensors respond in several tens of seconds and take several minutes for recovery [247]–[249]. The improved response may be attributed to the multi-scale porosity, which allows for fast diffusion to all active sites. The nanostructured SnO<sub>2</sub> film shows excellent sensing performance, even with low operating temperature on a miniaturized microheater platform.



**Figure 5.** (a) Sensitivity and (b) response and recovery time of the sensor at various operating temperatures.

#### 4. Conclusion

Here is presented a flexible and facile route for the localized growth of porous metal oxide films on a microheater platform to obtain high performance gas sensors. By sintering the suitable liquid-phase metal oxide precursor with a fast heating rate, a nanostructured metal oxide film with multi-length scale porosity can be generated directly on the fabricated microheater platform. The demonstrated SnO<sub>2</sub>-based CO sensor has low power consumption (~7 mW for 200 °C), low operating temperature (200 °C), low detection limit (~2 ppm CO), fast response time (<10 s) and recovery time (<30 s), and high sensitivity. More importantly, this facile fabrication strategy provides a way to manufacture high performance sensors with other types of metal oxides, and has the potential for low cost mass production.

## Chapter 9. Conclusions and Future Outlook

The development of more useful gas sensors can have a major impact on improving the health and safety of people and the environment. Because of the complexity involved in the detection of a particular gas *and* the amount at which it is present, there is no single solution or design that accomplishes the measurements needed in all applications. Therefore, there remains a strong need for research efforts to optimize gas sensing devices, including the development of transducer platforms, measurement techniques, and sensitive materials. One major effort involves decreasing the power consumption of heated sensor elements in order to enable their use in wireless sensor networks. Calorimetric or catalytic gas sensors requires a heated catalyst material that can promote the combustion of the gas of interest and a temperature sensitive element to detect the subsequent release of heat. Because of the high operating temperatures required to have appreciable reaction rates with existing catalytic materials based on noble metal nanoparticles, these sensor elements have high power consumption. Conductometric sensing measures the conductance of a sensitive material during gas exposure. Heating improves the response and recovery time of the sensor by increasing the rate of gas desorption. The use of a miniaturized heater platform fabricated with micromachining techniques helps to achieve low power consumption. In order to retain sensor performance in a smaller device, high surface area nanomaterials are used.

In this dissertation, a low-power microheater platform has been designed and fabricated using polycrystalline silicon as the heater material for moderate operating temperatures (200-400 °C) and silicon carbide for high operating temperatures (500 °C and above). Specific design choices have been made to facilitate sensing material deposition. Sensing materials have been selected based on the desired application. For calorimetric or catalytic gas sensing, high surface aerogels made of graphene and boron nitride have been loaded with catalytic noble metal nanoparticles. Hydrogen and propane sensing has been demonstrated with good sensitivity and very fast response and recovery time, thanks to the high thermal conductivity and minimal mass of the aerogel scaffold. Boron nitride aerogel provides higher thermal stability than graphene aerogel, which is useful at the operating temperatures required for propane detection. The silicon carbide microheater also improves the reliability of the propane measurement given its stability at high temperature. The fast thermal response of the microheater also allows for fast pulsed operation with no loss in sensitivity, such that the power consumption can be decreased by 10x while still collecting data every second. Selectivity can be achieved through the use of different catalytic materials in an array of sensors or through temperature scanning with a single sensor element.

Conductometric sensing for toxic gases is demonstrated with the high surface area aerogels as well. Graphene aerogel responds to a variety of gases such as nitrogen dioxide, carbon monoxide, and hydrogen at relevant concentration ranges. For certain gas combinations that have distinct thermal conductivity values, selectivity can be determined by collecting information from the microheater as well as the graphene aerogel. The graphene aerogel can also be engineered for improved selectivity towards nitrogen dioxide gas by coating with two-dimensional sheets of molybdenum disulfide. The success of this unique hybrid aerogel suggests that layered

combinations of two-dimensional materials connected into a high surface area 3D structure may offer improved sensing performance for other target gases and applications.

The thermal properties of the microheater even allow for the localized growth of a porous nanocrystalline tin oxide film with high sensitivity to carbon monoxide. The rapid anneal of liquid precursor to form the porous film in the exact location of the sensing electrodes is a technique that can be extended to other metal oxide chemistries and suggests a new method for manufacture of sensor elements.

Although progress has been made in the development of low-power sensor elements for combustible and toxic gas detection, further potential improvements remain. The microheater platform may benefit from the separation of the heating and temperature sensing functions, so that the materials can be optimized independently and the temperature sensor can provide closed loop control on the microheater operation. Following on the success of hydrogen and propane detection, methane would be a relevant target analyte due to its prevalence and its impact as a greenhouse gas. Further study, including optimization of the catalytic material, may reveal the key to enabling its detection. For the conductometric gas sensing, the complexity of the sensing mechanism requires additional investigation. With better understanding of the gas-solid interaction, more intelligent choice and faster evaluation of new materials can be conducted. Even with the improvement in stability with the switch from graphene to boron nitride sensing material and from polysilicon to silicon carbide microheater, the sensors have not yet been subject to the expected usage in commercial application. Response stability for at least one year would be expected, and in conditions with changing ambient temperature, humidity, vibration, and other factors. The microfabricated heater platform allows for multiple sensors on one chip in order to independently monitor several variables, thus enabling for compensation of factors such as temperature, humidity, and the presence of other gases. Future work demonstrating multiplexed sensing for more intelligent measurement will enable a wider array of applications. Ultimately, it is through continued research and development that low-power miniaturized gas sensors will enable detection of dangerous toxic and combustible gases for the improved protection of the environment and human health.

## Appendix 1. Methane Sensing

### 1. Motivation

There is a great deal of interest in low-power methane sensors, given that methane is so common and that methane leaks from industrial sources or releases from natural sources contribute heavily to climate change. Methane is indeed a more potent greenhouse gas than carbon dioxide, although its lifetime in the atmosphere is shorter [EPA]. Methane is also combustible and can explode when the concentration builds up to 5% in air [118].

The two main techniques for detecting methane are based on infrared and catalytic gas sensors. Electrochemical sensing for methane is not practical because the overpotential required for an appreciable methane reaction rate result in nearly every other gas oxidizing first, giving very poor selectivity. Infrared sensors detect the presence of C-H bond stretching to detect methane and other hydrocarbons, which gives them selectivity to at least a smaller group of potential gases. There are limitations to this type of sensor, including the ability to miniaturize the more complex components, the expensive of the more complex components, and the susceptibility to humidity and particulate matter in air. Catalytic gas sensors are also not particularly selective to methane, but tend to be simpler and cheaper in operation and manufacture [1]. As described in Chapter 1, the sensor functions by heating a catalytic material that catalyzes the reaction of the target gas with oxygen, which releases heat. The released heat is detected as a resistance change due to the increased temperature of the sensing element. Required operating temperatures are 450 °C and above. Microheater-based methane sensors would offer low power consumption compared to typical pellistor technology [155].

Several groups have reported microheater-based methane sensors, as summarized in Table 1. These are largely based on platinum or palladium catalysts on alumina supports. More recent advancements have lead to sensor elements with power consumption on the order of 25 to 35 mW and sensitivity similar to commercially available elements (~15 mV per % CH<sub>4</sub>) [Brauns]. Given the improvements reported in previous chapters of the aerogel-based catalytic materials and the importance of methane as a target gas, it seemed reasonable to attempt to detect methane using the low-power catalytic gas sensors developed for hydrogen and propane. However, as will be elucidated here, all attempts proved unsuccessful.

**Table 1.** MEMS-based catalytic methane sensors reported in literature

| Ref.  | Catalyst material                                      | Power [mW] | Methane Conc. Range [%] | Sensitivity [mV/% CH <sub>4</sub> ] |
|-------|--------------------------------------------------------|------------|-------------------------|-------------------------------------|
| [109] | Pd-Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>        | 35         | 0.17 – 2.45%            | 14.5                                |
| [257] | 15 wt% Pd-Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | 28         | 0.4 – 3.6%              | 2                                   |
| [17]  | Pt/Al <sub>2</sub> O <sub>3</sub>                      | 50         | 0.8 – 3.2%              | 18                                  |
| [30]  | 15 wt% Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>    | 25         | 0.4 – 3.6%              | 12                                  |
| [258] | Pd/Al <sub>2</sub> O <sub>3</sub>                      | 50         | 2.5%                    | 10                                  |
| [19]  | Pt/Al <sub>2</sub> O <sub>3</sub>                      | 400        | 0.1 – 1%                | 22                                  |
| [18]  | Pd/Al <sub>2</sub> O <sub>3</sub>                      | 6,900      | 0.3 – 4%                | 6                                   |

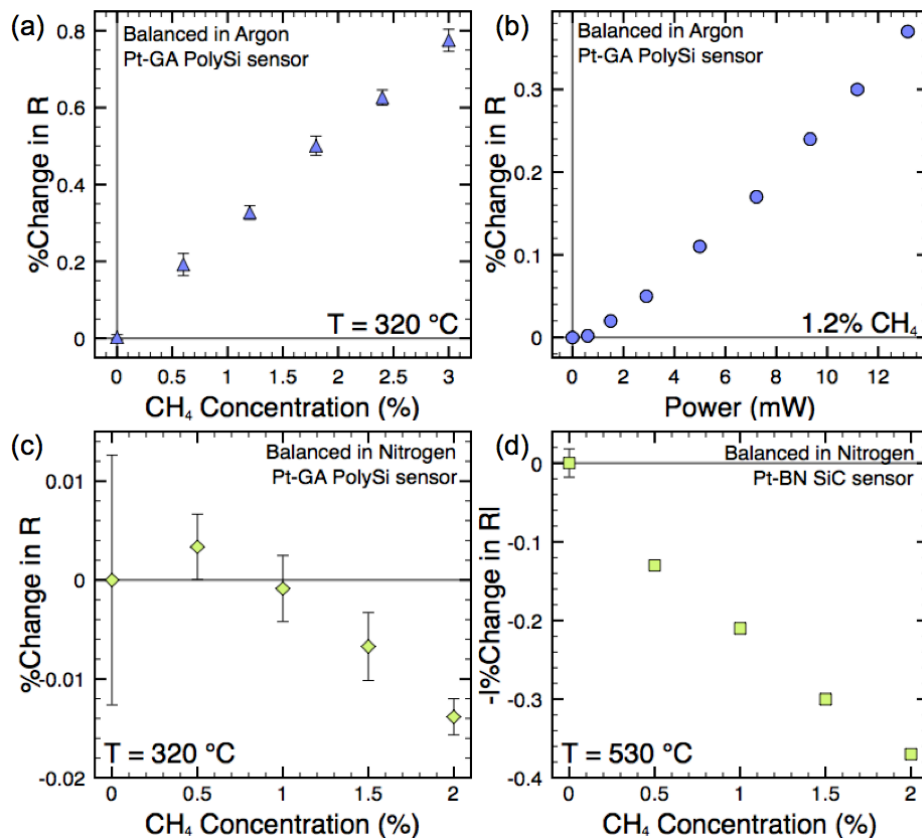


## 2. Experimental Results

Early testing with methane using the Pt-GA polysilicon microheater sensor seemed to give some results (Figure 1a). But upon further investigation, the response was found to be due to the methane tank being balanced in argon, which changed the thermal conductivity of the gas stream being fed to the sensor. The thermal conductivity of argon is  $0.016 \text{ W m}^{-1} \text{ K}^{-1}$  compared to  $0.024 \text{ W m}^{-1} \text{ K}^{-1}$  for air and  $0.03 \text{ W m}^{-1} \text{ K}^{-1}$  for methane. Because the tank is dilute in methane (5%), as the methane concentration is increased, the proportion of argon in the stream increased, decreasing the overall thermal conductivity. Since the microheater conducts heat to the surrounding gas, the effect is that the temperature of the microheater increases as it conducts less heat to the surrounding gas. This results in the resistance increase with increasing concentration in Figure 1a, which looks like a response to the exothermic combustion of methane. The discovery of the argon problem was made by observing the same response when balancing the stream in nitrogen instead of air. With no oxygen present, there should be no methane combustion response, so the fact that the same resistance change in the heater was observed signaled that there was a different source of the resistance change. Furthermore, the response occurred even at low temperatures, much lower than expected for methane combustion, and the sensitivity increased linearly with temperature (Figure 1b). The methane reaction rate should have an exponential relationship with temperature until it reaches a mass transfer limited regime where it should plateau.

A new tank of methane gas balanced in nitrogen was purchased and used for subsequent testing (Figure 1c). There is a slight decrease in the response as the methane concentration increases, in this case because the addition of methane increases the thermal conductivity of the stream. Even using more thermally stable materials (Pt-BN on silicon carbide microheater) and a higher operating temperature, only the thermal conductivity response is visible (Figure 1d). Additionally, the response does not change when there is no oxygen present.

The sensors can detect hydrogen and propane gas with good sensitivity, thus it is possible that the stability of the methane molecule makes it impossible to detect. Methane combustion should release more heat per Joule than hydrogen gas ( $802 \text{ kJ mol}^{-1}$  for methane versus  $244 \text{ kJ mol}^{-1}$  for hydrogen), which is possible to detect even at temperatures around  $300^\circ\text{C}$ . However, if the rate of reaction for methane combustion is much lower than hydrogen or propane combustion, then the methane will not be detected.



**Figure 1.** (a) Change in microheater resistance for Pt-GA polysilicon microheater versus methane concentration with methane tank balanced in argon. (b) Change in microheater resistance at 1.2% methane at various power levels, also balanced in argon. (c) Change in microheater resistance versus methane concentration with methane tank balanced in nitrogen, showing no response. (d) Using Pt-BN SiC sensor at a higher temperature with methane tank balanced in nitrogen still shows only a thermal conductivity response. The negative response is plotted since SiC microheater has opposite TCR relationship of polysilicon.

There are several possible reasons why methane combustion is not observed, even at similar temperatures to other reported sensors (Table 1). The first is that the smaller size of the microheater limits the possible catalyst loading below the required level to generate enough heat to be detectable. A theoretical analysis follows that shows this may be the case. Additional differences may be due to the catalyst material. Most other works use platinum on a metal oxide support, and it may be that the platinum interaction with the support assists with the methane oxidation reaction. The platinum nanoparticle sizes are not reported for the works in Table 1, but it is possible that there is a size difference that impacts the methane oxidation reaction rate as well. There are reports demonstrating that the presence of chlorine ions severely hinders the methane oxidation rate [8]. The platinum precursor used to load the graphene and boron nitride aerogels is chlorinated and it may be possible that in the reduction process, not all of this chlorine is removed. Although other works in Table 1 also use the same precursors, the detail of the reduction processes they use may be different. All of this suggests the importance of reporting the details of the catalytic material used in these types of gas sensors.

### 3. Theoretical analysis

Using a combination of experimental results from the microheater platform in conjunction with methane combustion rates on platinum catalysts from the literature allows the minimum required catalyst amount to be calculated. First, from the microheater platform, the minimum detectable signal is calculated in the same way as the theoretical limit of detection, from the average and standard deviation of the baseline. For the microheater device in question, when powered to 450 °C (4.8 V), the average baseline resistance is 1813.5  $\Omega$  and the standard deviation is  $\pm 0.05 \Omega$ . Using a signal to noise limit of 3, the minimum detectable resistance is 1813.65  $\Omega$ . The power input to achieve this change in resistance can be calculated from the plot of resistance versus power consumption, so the 0.15  $\Omega$  increase in resistance correlates to a 0.05 mW power input to the microheater from the catalyst during methane combustion. This represents the minimum detectable power input that would be required from the reaction of methane on the platinum nanoparticle catalyst and subsequent transfer to the microheater. Since the exact heat transfer from the nanoparticles supported in the aerogel to the microheater is very difficult to quantify, for a minimum case, it can be assumed that the heat transfer is perfect (no losses).

From the catalysis literature, there are several reports for the reaction rates for methane oxidation on platinum catalysts, primarily supported on alumina [6], [259]–[261], although there are some studies investigating the effect of various metal oxide supports on methane [262] and propane oxidation [263]. The reaction rates are summarized in Table 2 with the corresponding catalyst weight, support, temperatures, and oxygen conditions.

Given these reaction rates, the heat of combustion for methane, and the minimum detectable power input assuming no heat transfer losses, a minimum required mass of catalyst can be calculated (Table 2) from the following relationship:

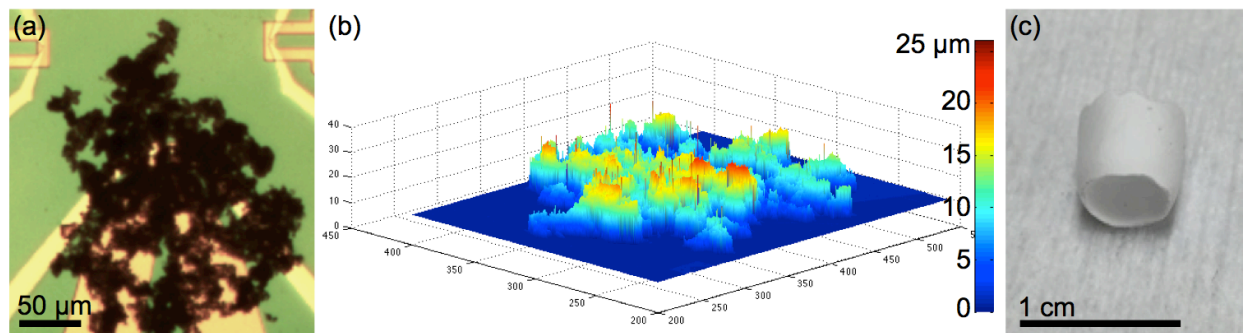
$$\text{Catalyst Rxn Rate} * \Delta H^{\circ}_{\text{Methane}} * m_{\text{catalyst}} = \text{Power} \quad (1)$$

For those rates given per surface atom of platinum, the surface area of platinum is converted to a mass assuming  $10^{15}$  atoms  $\text{cm}^{-2}$  at the surface, nanoparticles with an average diameter of 2 nm, and a platinum density of 21.45  $\text{g cm}^{-3}$ . Given the variation in reported reaction rate, the minimum required platinum mass is calculated to be on the order of  $10^{-4}$  to  $10^{-8}$  g, although it should be noted that the lowest mass comes from a reaction rate in low oxygen conditions, which is not as relevant to the sensor operation.

**Table 2.** Methane oxidation reaction rates on various platinum catalysts and subsequent calculated minimum Pt catalyst mass

| Ref.  | Catalyst                               | T (°C) | Oxygen ratio<br>[O <sub>2</sub> ]:[CH <sub>4</sub> ] | Reaction rate                                                                     | Mass of<br>catalyst (g) |
|-------|----------------------------------------|--------|------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------|
| [261] | 2.7% Pt/Al <sub>2</sub> O <sub>3</sub> | 410    | 0.45:1                                               | 296 mmol min <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup>                         | 1.26 x 10 <sup>-8</sup> |
| [259] | 0.2% Pt/Al <sub>2</sub> O <sub>3</sub> | 450    | 2:1                                                  | 0.023 mmol min <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup>                       | 1.63 x 10 <sup>-4</sup> |
| [260] | 0.1% Pt/Al <sub>2</sub> O <sub>3</sub> | 450    | 2:1                                                  | 0.01 mmol min <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup>                        | 3.74 x 10 <sup>-4</sup> |
| [260] | 2% Pt/Al <sub>2</sub> O <sub>3</sub>   | 450    | 2:1                                                  | 0.16 mmol min <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup>                        | 2.34 x 10 <sup>-5</sup> |
| [6]   | 4% Pt/Al <sub>2</sub> O <sub>3</sub>   | 450    | 5:1                                                  | 0.013 molecules CH <sub>4</sub> s <sup>-1</sup><br>surface Pt atoms <sup>-1</sup> | 2.06 x 10 <sup>-6</sup> |

Next, the actual deposited mass of platinum on a microheater can be estimated. Figure 2a shows an optical image of a microheater sample with platinum nanoparticle-loaded boron nitride aerogel deposited on top. Using confocal microscopy (Olympus LEXT OLS3000), a three-dimensional scan of the chip can be taken (Figure 2b) and plotted with MATLAB. By integrating the area under the curve, the deposited volume of aerogel is calculated to be  $245,000 \mu\text{m}^3$ . From measurements done on a cylindrical disk of the boron nitride aerogel (Figure 2c), the density is calculated to be  $0.069 \text{ g cm}^{-3}$ . After platinum loading, the mass of the cylindrical disk increases by 80% while the volume remains the same. Assuming uniform loading of platinum, such that the aerogel deposited on the chip has the same weight percent platinum as the bulk cylindrical disk, then the calculated mass of platinum deposited on the microheater comes to about  $10^{-8} \text{ g}$ . This is lower than the range of minimum required platinum calculated from the reaction rates, so it is reasonable to conclude that given the reaction rate of methane oxidation on platinum, there is not enough platinum loaded onto the microheater to allow for methane detection. The calculation of  $1.36 \times 10^{-8}$  also does not factor in the catalyst temperature. Given the small size of the microheater heated area compared to the aerogel loading, it is possible that the farthest edges of the aerogel will be much cooler than the center, giving an even lower reaction rate at those catalyst sites.



**Figure 2.** (a) Optical image of the boron nitride aerogel loaded on a polysilicon microheater. (b) 3D map of aerogel from (a) taken with confocal microscope. Color height scale from 0 to 25  $\mu\text{m}$ . Axis units are also in  $\mu\text{m}$ . (c) Optical image of boron nitride aerogel disk after synthesis.

The same analysis shows that propane oxidation should be possible using reaction rates for platinum supported on alumina [264]. Even at a lower temperature of  $290^\circ\text{C}$ , the reaction rate is  $203 \text{ mmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$ , and when using the higher combustion energy of propane ( $2044 \text{ kJ mol}^{-1}$ ), the minimum mass of platinum needed is  $7.2 \times 10^{-9} \text{ g}$ . Given the magnitude of assumptions, the order of magnitude is more useful than the absolute value calculated, and in this case, the minimum mass of platinum is on the same order as the calculated platinum mass for the aerogel loaded on the microheater in Figure 2a. The fact that the propane detection is observed experimentally and is theoretically possible given this analysis, lends some more confidence to the analysis as well.

#### 4. Conclusions

Although MEMS-based catalytic methane sensors had been previously reported, our catalytic gas sensors based on platinum nanoparticle-loaded aerogels and a small, low-power polysilicon or silicon carbide microheater do not show any methane response. Given the lower reaction rate for

methane on platinum, it may be necessary to increase the catalytic surface area inside the aerogel through higher loading or smaller nanoparticle size. Palladium nanoparticles tend to show higher activity for methane in oxygen-rich conditions, so palladium nanoparticle-loaded aerogels could be a more successful catalyst material choice. Removal of chlorine from the metal precursors may also assist with improving the methane oxidation rate. If the platinum-support interaction proves to be important, then the catalyst support could be changed to high surface area metal oxides or even zeolites. Ultimately, these efforts illuminate the importance of thorough characterization of the catalytic materials used for these types of gas sensors.

## Bibliography

- [1] I. Bársony, C. Dücső, and P. Fürjes, "Thermometric Gas Sensing," in *Solid State Gas Sensing*, E. Comini, G. Faglia, and G. Sberveglieri, Eds. Boston, MA: Springer US, 2009, pp. 237–260.
- [2] J. B. Miller, "Catalytic Sensors for Monitoring Explosive Atmospheres," *IEEE Sens. J.*, vol. 1, no. 1, pp. 88–93, 2001.
- [3] M. S. A. Company, *Gas Detection Handbook*, 5th ed. Pittsburgh, PA, 2007.
- [4] E. A. Symons, "Catalytic Gas Sensors," in *Gas Sensors: Principles, Operation and Developments*, Dordrecht: Kluwer Academic Publishers, 1992, pp. 169–185.
- [5] J. Chou, "Catalytic Combustible Gas Sensors," in *Hazardous Gas Monitors*, New York, NY: McGraw-Hill, 2000, pp. 37–45.
- [6] R. Burch and P. K. Loader, "Investigation of Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts for the combustion of methane at low concentrations," *Appl. Catal. B Environ.*, vol. 5, pp. 149–164, 1994.
- [7] T. V. Choudhary, S. Banerjee, and V. R. Choudhary, "Catalysts for combustion of methane and lower alkanes," *Appl. Catal. A Gen.*, vol. 234, pp. 1–23, 2002.
- [8] P. Gélin and M. Primet, "Complete oxidation of methane at low temperature over noble metal based catalysts: a review," *Appl. Catal. B Environ.*, vol. 39, no. 1, pp. 1–37, Nov. 2002.
- [9] M. Gall, "The Si Planar Pellistor: a Low-power Pellistor Sensor in Si Thin-Film Technology," *Sensors Actuators B Chem.*, vol. 4, pp. 533–538, 1991.
- [10] M. Gall, "The Si-Planar-Pellistor array, a detection unit for combustible gases," *Sensors Actuators B Chem.*, vol. 15–16, pp. 260–264, 1993.
- [11] P. Krebs and A. Grisel, "A low power integrated catalytic gas sensor," *Sensors Actuators B Chem.*, vol. 13–14, pp. 155–158, 1993.
- [12] A. Hierlemann, O. Brand, C. Hagleitner, and H. Baltes, "Microfabrication techniques for chemical/biosensors," *Proc. IEEE*, vol. 91, no. 6, pp. 839–863, Jun. 2003.
- [13] R. P. Manginell, J. H. Smith, and A. J. Ricco, "Overview of micromachined platforms for thermal sensing and gas detection," *Smart Struct. Mater. 1997 Smart Electron. MEMS*, vol. 3046, no. 1, pp. 273–284, 1997.
- [14] G. Sberveglieri, W. Hellmich, and G. Müller, "Silicon hotplates for metal oxide gas sensor elements," *Microsyst. Technol.*, vol. 3, no. 4, pp. 183–190, 1997.

- [15] I. Bársony, M. Ádám, P. Fürjes, R. Lucklum, M. Hirschfelder, S. Kulinyi, and C. Dücső, "Efficient catalytic combustion in integrated micropellistors," *Meas. Sci. Technol.*, vol. 20, p. 124009, Dec. 2009.
- [16] L. Xu, T. Li, X. Gao, and Y. Wang, "Development of a reliable micro-hotplate with low power consumption," *IEEE Sens. J.*, vol. 11, no. 4, pp. 913–919, Apr. 2011.
- [17] S. Kulinyi, D. Brandszájsz, H. Amine, M. Ádám, P. Fürjes, I. Bársony, and C. Dücső, "Olfactory detection of methane, propane, butane and hexane using conventional transmitter norms," *Sensors Actuators B Chem.*, vol. 111–112, pp. 286–292, Nov. 2005.
- [18] A. Chen, R. Luo, T. C. Tan, and C. C. Liu, "A thick-film calorimetric sensor for monitoring the concentration of combustible gases," *Sensors and Actuators*, vol. 19, no. 3, pp. 237–248, 1989.
- [19] J. S. Lee, J. W. Park, and S. M. Shin, "Fabrication of a micro catalytic gas sensor using thin film process and Si anisotropic etching techniques," *Sensors Actuators B Chem.*, vol. 45, no. 3, pp. 265–269, Dec. 1997.
- [20] D. Briand, F. Beaudoin, J. Courbat, N. F. de Rooij, R. Desplats, and P. Perdu, "Failure analysis of micro-heating elements suspended on thin membranes," *Microelectron. Reliab.*, vol. 45, no. 9–11, pp. 1786–1789, Sep. 2005.
- [21] H. M. Chuang, K. B. Thei, S. F. Tsai, and W. C. Liu, "Temperature-dependent characteristics of polysilicon and diffused resistors," *IEEE Trans. Electron Devices*, vol. 50, no. 5, pp. 1413–1415, 2003.
- [22] V. K. Khanna, M. Prasad, V. K. Dwivedi, C. Shekhar, A. C. Pankaj, and J. Basu, "Design and electro-thermal simulation of a polysilicon microheater on a suspended membrane for use in gas sensing," *Indian J. Pure Appl. Phys.*, vol. 45, pp. 332–335, 2007.
- [23] A. D. McConnell, S. Uma, and K. E. Goodson, "Thermal conductivity of doped polysilicon layers," *J. Microelectromechanical Syst.*, vol. 10, no. 3, pp. 360–369, 2001.
- [24] P. Fürjes, M. Ádám, C. Dücső, J. Zettner, I. Bársony, C. Dücső, J. Zettner, and I. Bársony, "Thermal effects by the sensitive coating of calorimetric gas sensors," *Sensors Actuators B Chem.*, vol. 111–112, no. SUPPL., pp. 96–101, Nov. 2005.
- [25] E. Brauns, E. Morsbach, G. Schnurpfeil, M. Bäumer, and W. Lang, "A miniaturized catalytic gas sensor for hydrogen detection based on stabilized nanoparticles as catalytic layer," *Sensors Actuators B Chem.*, vol. 187, pp. 420–425, Oct. 2013.
- [26] E. Brauns, E. Morsbach, G. Schnurpfeil, M. Bäumer, and W. Lang, "A fast and sensitive catalytic gas sensors for hydrogen detection based on stabilized nanoparticles as catalytic layer," *Sensors Actuators, B Chem.*, vol. 193, pp. 895–903, Mar. 2014.



- [27] E. Morsbach, E. Brauns, T. Kowalik, W. Lang, S. Kunz, and M. Bäumer, “Ligand-stabilized Pt nanoparticles (NPs) as novel materials for catalytic gas sensing: influence of the ligand on important catalytic properties,” *Phys. Chem. Chem. Phys.*, vol. 16, no. 39, pp. 21243–51, 2014.
- [28] E. Vereshchagina, R. A. M. Wolters, and J. G. E. Gardeniers, “Measurement of reaction heats using a polysilicon-based microcalorimetric sensor,” *Sensors Actuators, A Phys.*, vol. 169, no. 2, pp. 308–316, 2011.
- [29] R. E. Cavicchi, G. E. Poirier, N. H. Tea, M. Afridi, D. Berning, a. Hefner, J. Suehle, M. Gaitan, S. Semancik, and C. Montgomery, “Micro-differential scanning calorimeter for combustible gas sensing,” *Sensors Actuators B Chem.*, vol. 97, no. 1, pp. 22–30, Jan. 2004.
- [30] L. Xu, Y. Y. Wang, H. Zhou, Y. Liu, T. Li, and Y. Y. Wang, “Design, fabrication, and characterization of a high-heating-efficiency 3-D microheater for catalytic gas sensors,” *J. Microelectromechanical Syst.*, vol. 21, no. 6, pp. 1402–1409, 2012.
- [31] M. Gardon and J. M. Guilemany, “A review on fabrication, sensing mechanisms and performance of metal oxide gas sensors,” *J. Mater. Sci. Mater. Electron.*, vol. 24, no. 5, pp. 1410–1421, 2013.
- [32] J. Watson, “The tin oxide gas sensor and its applications,” *Sensors and Actuators*, vol. 5, no. 1, pp. 29–42, 1984.
- [33] K. Ihokura and J. Watson, *The Stannic Oxide Gas Sensor: Principles and Applications*. CRC Press, 1994.
- [34] H.-J. Kim and J.-H. Lee, “Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview,” *Sensors Actuators B Chem.*, vol. 192, pp. 607–627, 2014.
- [35] S. Chang, “Oxygen chemisorption on tin oxide: Correlation between electrical conductivity and EPR measurements,” *J. Vac. Sci. Technol.*, vol. 17, no. 1, pp. 366–369, Jan. 1980.
- [36] N. Barsan and U. Weimar, “Conduction model of metal oxide gas sensors,” *J. Electroceramics*, vol. 7, no. 3, pp. 143–167, 2001.
- [37] N. Yamazoe, J. Fuchigami, M. Kishikawa, and T. Seiyama, “Interactions of tin oxide surface with O<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>,” *Surf. Sci.*, vol. 86, pp. 335–344, 1979.
- [38] N. Yamazoe, “New approaches for improving semiconductor gas sensors,” *Sensors Actuators B Chem.*, vol. 5, no. 1–4, pp. 7–19, Aug. 1991.
- [39] A. K. Geim and K. S. Novoselov, “The rise of graphene,” *Nat. Mater.*, vol. 6, no. 3, pp. 183–91, Mar. 2007.

- [40] S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutiérrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, and J. E. Goldberger, "Progress, challenges, and opportunities in two-dimensional materials beyond graphene," *ACS Nano*, vol. 7, no. 4, pp. 2898–926, 2013.
- [41] S. S. Varghese, S. Lonkar, K. K. Singh, S. Swaminathan, and A. Abdala, "Recent advances in graphene based gas sensors," *Sensors Actuators B Chem.*, vol. 218, pp. 160–183, 2015.
- [42] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, "Detection of individual gas molecules adsorbed on graphene," *Nat. Mater.*, vol. 6, no. 9, pp. 652–5, Sep. 2007.
- [43] W. Li, X. Geng, Y. Guo, J. Rong, Y. Gong, L. Wu, X. Zhang, P. Li, J. Xu, G. Cheng, M. Sun, and L. Liu, "Reduced graphene oxide electrically contacted graphene sensor for highly sensitive nitric oxide detection," *ACS Nano*, vol. 5, no. 9, pp. 6955–6961, 2011.
- [44] J. W. Suk, W. H. Lee, J. Lee, H. Chou, R. D. Piner, Y. Hao, D. Akinwande, and R. S. Ruoff, "Enhancement of the electrical properties of graphene grown by chemical vapor deposition via controlling the effects of polymer residue," *Nano Lett.*, vol. 13, pp. 1462–1467, 2013.
- [45] F. Ricciardella, E. Massera, T. Polichetti, M. L. Miglietta, and G. Di Francia, "A calibrated graphene-based chemi-sensor for sub parts-per-million NO<sub>2</sub> detection operating at room temperature," *Appl. Phys. Lett.*, vol. 104, p. 183502, 2014.
- [46] A. Zöpfl, M.-M. Lemberger, M. König, G. Ruhl, F.-M. Matysik, and T. Hirsch, "Reduced graphene oxide and graphene composite materials for improved gas sensing at low temperature," *Faraday Discuss.*, vol. 173, pp. 403–414, 2014.
- [47] G. Lu, L. E. Ocola, and J. Chen, "Reduced graphene oxide for room-temperature gas sensors," *Nanotechnology*, vol. 20, no. 44, p. 445502, 2009.
- [48] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang, and H. Zhang, "Fabrication of single- and multilayer MoS<sub>2</sub> film-based field-effect transistors for sensing NO at room temperature," *Small*, vol. 8, no. 1, pp. 63–7, Jan. 2012.
- [49] Q. He, Z. Zeng, Z. Yin, H. Li, S. Wu, X. Huang, and H. Zhang, "Fabrication of flexible MoS<sub>2</sub> thin-film transistor arrays for practical gas-sensing applications," *Small*, vol. 8, no. 19, pp. 2994–9, Oct. 2012.
- [50] K. Lee, R. Gatensby, N. McEvoy, T. Hallam, and G. S. Duesberg, "High-performance sensors based on molybdenum disulfide thin films," *Adv. Mater.*, vol. 25, no. 46, pp. 6699–702, Dec. 2013.

- [51] H. Choi, J. S. Choi, J. S. Kim, J. H. Choe, K. H. Chung, J. W. Shin, J. T. Kim, D. H. Youn, K. C. Kim, J. I. Lee, S. Y. Choi, P. Kim, C. G. Choi, and Y. J. Yu, "Flexible and transparent gas molecule sensor integrated with sensing and heating graphene layers," *Small*, pp. 3685–3691, 2014.
- [52] J. W. Gardner, M. T. Cole, A. De Luca, P. Clément, E. Llobet, S. Z. Ali, and F. Udreă, "Graphene SOI CMOS sensors for detection of ppb levels of NO<sub>2</sub> in air," *Transducers '13*, no. June, pp. 2055–2058, 2013.
- [53] D. J. Late, Y.-K. Huang, B. Liu, J. Acharya, S. N. Shirodkar, J. Luo, A. Yan, D. Charles, U. V. Waghmare, V. P. Dravid, and C. N. R. Rao, "Sensing behavior of atomically thin-layered MoS<sub>2</sub> transistors," *ACS Nano*, vol. 7, no. 6, pp. 4879–4891, Jun. 2013.
- [54] M. Donarelli, S. Prezioso, F. Perrozzi, F. Bisti, M. Nardone, L. Giancaterini, C. Cantalini, and L. Ottaviano, "Response to NO<sub>2</sub> and other gases of resistive chemically exfoliated MoS<sub>2</sub>-based gas sensors," *Sensors Actuators B Chem.*, vol. 207, pp. 602–613, Feb. 2015.
- [55] J. A. Robinson, E. S. Snow, S. C. Badescu, T. L. Reinecke, and F. K. Perkins, "Role of defects in single-walled carbon nanotube chemical sensors," *Nano Lett.*, vol. 6, no. 8, pp. 1747–51, Aug. 2006.
- [56] R. K. Paul, S. Badhulika, N. M. Saucedo, and A. Mulchandani, "Graphene nanomesh as highly sensitive chemiresistor gas sensor," *Anal. Chem.*, vol. 84, no. 19, pp. 8171–8, Oct. 2012.
- [57] U. Latif and F. Dickert, "Graphene Hybrid Materials in Gas Sensing Applications," *Sensors*, vol. 15, no. 12, pp. 30504–30524, 2015.
- [58] J. Watson, "A note on the electrical characterization of solid-state gas sensors," *Sensors Actuators B Chem.*, vol. 8, pp. 173–177, 1992.
- [59] A. Shrivastava and V. B. Gupta, "Methods for the determination of limit of detection and limit of quantitation of the analytical methods," *Chronicles Young Sci.*, vol. 2, no. 1, pp. 21–25, Jan. 2011.
- [60] D. Briand, A. Krauss, B. van der Schoot, U. Weimar, N. Barsan, W. Gopel, and N. F. de Rooij, "Design and fabrication of high-temperature micro-hotplates for drop-coated gas sensors," *Sensors Actuators B Chem.*, vol. 68, pp. 223–233, 2000.
- [61] J. Courbat, D. Briand, and N. F. de Rooij, "Reliability improvement of suspended platinum-based micro-heating elements," *Sensors Actuators A Phys.*, vol. 142, no. 1, pp. 284–291, Mar. 2008.
- [62] P. Bhattacharyya, "Technological journey towards reliable microheater development for MEMS gas sensors: a review," *IEEE Trans. Device Mater. Reliab.*, vol. 14, no. 2, pp. 589–599, 2014.

- [63] P. S. Ho and T. Kwok, "Electromigration in metals," *Reports Prog. Phys.*, vol. 52, p. 301, 1989.
- [64] R. Hamilton, "NanoSpec Manual," *EECS 143 Microfabrication Technology*. UC Berkeley, pp. 2–4, 1996.
- [65] A. K. Sinha, H. J. Levinstein, and T. E. Smith, "Thermal stresses and cracking resistance of dielectric films (SiN, Si<sub>3</sub>N<sub>4</sub>, and SiO<sub>2</sub>) on Si substrates," *J. Appl. Phys.*, vol. 49, no. 4, pp. 2423–2426, 1978.
- [66] M. F. Doerner, D. S. Gardner, and W. D. Nix, "Plastic properties of thin films on substrates as measured by submicron indentation hardness and substrate curvature techniques," *J. Mater. Res.*, vol. 1, no. 6, pp. 845–851, 1986.
- [67] F. M. Smits, "Measurements of sheet resistivity with the four-point probe," *Bell Syst Tech J*, vol. 37, no. 3, pp. 711–718, 1958.
- [68] K. R. Williams, K. Gupta, and M. Wasilik, "Etch rates for micromachining processing - part II," *J. Microelectromechanical Syst.*, vol. 12, no. 6, pp. 761–778, 2003.
- [69] L. P. Howard and S. T. Smith, "A metrological constant force stylus profiler," *Rev. Sci. Instrum.*, vol. 65, no. 4, p. 892, Apr. 1994.
- [70] "Alpha-Step IQ, PO-ASIQ3-11/10," *Development Series*. KLA-Tencor Corporation, pp. 1–2, 2010.
- [71] H. Seidel, L. Csepregi, A. Heuberger, and H. Baumgärtel, "Anisotropic Etching of Crystalline Silicon in Alkaline Solutions," *J. Electrochem. Soc.*, vol. 137, no. 11, pp. 249–260, 1990.
- [72] I. C. Chen, S. E. Holland, and C. Hu, "Electrical Breakdown in Thin Gate and Tunneling Oxides," *IEEE Trans. Electron Devices*, vol. 32, no. 2, pp. 413–422, 1985.
- [73] M. Mongillo, P. Spathis, G. Katsaros, P. Gentile, M. Sanquer, and S. De Franceschi, "Joule-assisted silicidation for short-channel silicon nanowire devices," *ACS Nano*, vol. 5, no. 9, pp. 7117–7123, 2011.
- [74] K. Kato, T. Ono, and Y. Amemiya, "A physical mechanism of current-induced resistance decrease in heavily doped polysilicon resistors," *IEEE Trans. Electron Devices*, vol. 29, no. 8, pp. 1156–1161, 1982.
- [75] J. E. Suarez, B. E. Johnson, and B. El-Kareh, "Thermal stability of polysilicon resistors," *IEEE Trans. Components, Hybrids, Manuf. Technol.*, vol. 15, no. 3, pp. 386–392, 1992.
- [76] Z. Bendekovic, P. Biljanovic, and D. Grgec, "Polysilicon temperature sensor," *MELECON '98. 9th Mediterr. Electrotech. Conf. Proc.*, vol. 1, pp. 362–366, 1998.

- [77] M. Ehmann, P. Ruther, M. von Arx, and O. Paul, "Operation and short-term drift of polysilicon-heated CMOS microstructures at temperatures up to 1200 K," *J. Micromechanics Microengineering*, vol. 11, no. 4, pp. 397–401, Jul. 2001.
- [78] M. Ehmann, F. Schubert, P. Ruther, and O. Paul, "Thermally activated ageing of polysilicon," *IEEE Sensors*, vol. 1, pp. 601–606, 2002.
- [79] Q. Zhou, A. Sussman, J. Chang, J. Dong, A. Zettl, and W. Mickelson, "Fast response integrated MEMS microheaters for ultra low power gas detection," *Sensors Actuators, A Phys.*, vol. 223, pp. 67–75, 2015.
- [80] R. F. Barron, *Cryogenic Heat Transfer*. CRC Press, 1999.
- [81] M. T. Bensidhoum, M. Laghrouche, A. Sidi Said, L. Montes, and J. Boussey, "Fabrication flaws and reliability in MEMS thin film polycrystalline flow sensor," *Microsyst. Technol.*, vol. 20, no. 1, pp. 1–7, Nov. 2013.
- [82] M. Y. Afridi, J. S. Suehle, D. W. Berning, A. R. Hefner, R. E. Cavicchi, S. Semancik, C. B. Montgomery, and C. J. Taylor, "A monolithic CMOS microhotplate-based gas sensor system," *IEEE Sens. J.*, vol. 2, no. 6, pp. 644–655, 2002.
- [83] C. H. Mastrangelo, J. H. J. Yeh, and R. S. Muller, "Electrical And Optical Characteristics Of Vacuum-Sealed Polysilicon Microlamps," *IEEE Trans. Electron Devices*, vol. 39, no. 6, pp. 1363–1375, 1992.
- [84] J. Belmonte, J. Puigcorbe, J. Arbiol, A. Vila, J. R. Morante, N. Sabate, I. Grecia, and C. Cane, "High-temperature low-power performing micromachined suspended micro-hotplate for gas sensing applications," *Sensors Actuators, B Chem.*, vol. 114, no. 2, pp. 826–835, 2006.
- [85] J. Lee, J. Park, J.-S. Park, H.-D. Park, and S.-M. Shin, "Effects of deposition conditions on physical properties and stresses of Pt and (Al, Si)Ox thin films," *J. Mater. Sci. Lett.*, vol. 16, pp. 941–945, 1997.
- [86] J. Lee, H.-D. Park, S.-M. Shin, and J. Park, "Agglomeration phenomena of high temperature coefficient of resistance platinum films deposited by electron beam evaporation," *J. Mater. Sci. Lett.*, vol. 16, pp. 1257–1259, 1997.
- [87] M. Abdel-Rahman, S. Ilahi, M. F. Zia, M. Alduraibi, N. Debbbar, N. Yacoubi, and B. Ilahi, "Temperature coefficient of resistance and thermal conductivity of Vanadium oxide 'Big Mac' sandwich structure," *Infrared Phys. Technol.*, vol. 71, pp. 127–130, 2015.
- [88] W. Buttner, R. Burgess, M. Post, and C. Rivkin, "Summary and Findings from the NREL/DOE Hydrogen Sensor Workshop," 2011.
- [89] T. Hübert, L. Boon-Brett, G. Black, and U. Banach, "Hydrogen sensors - A review," *Sensors Actuators, B Chem.*, vol. 157, no. 2, pp. 329–352, 2011.

- [90] M. Kimura and N. Takashima, "MEMS Hydrogen Gas Sensor for the Entire Concentration Range of Hydrogen Gas," *Sensors Mater.*, vol. 23, no. 7, pp. 419–434, 2011.
- [91] I. Simon and M. Arndt, "Thermal and gas-sensing properties of a micromachined thermal conductivity sensor for the detection of hydrogen in automotive applications," *Sensors Actuators A Phys.*, vol. 97–98, pp. 104–108, Apr. 2002.
- [92] G. Korotcenkov, S. Do Han, and J. R. Stetter, "Review of electrochemical hydrogen sensors," *Chem. Rev.*, vol. 109, no. 3, pp. 1402–33, Mar. 2009.
- [93] J. R. Stetter and J. Li, "Amperometric gas sensors--a review.," *Chem. Rev.*, vol. 108, no. 2, pp. 352–66, Feb. 2008.
- [94] V. Aroutiounian, "Metal oxide hydrogen, oxygen, and carbon monoxide sensors for hydrogen setups and cells," *Int. J. Hydrogen Energy*, vol. 32, no. 9, pp. 1145–1158, Jun. 2007.
- [95] S. Yu, U. Welp, L. Hua, A. Rydh, W. Kwok, and H. H. Wang, "Fabrication of Palladium Nanotubes and Their Application in Hydrogen Sensing," *Chem. Mater.*, vol. 17, pp. 3445–3450, 2005.
- [96] M. Daughtery, D. Haberman, C. Salter, D. Benson, and B. Hoffheins, "Low Cost Hydrogen Sensors for Hydrogen Fuel Safety," in *Proc. of the 1999 U.S. DOE Hydrogen Program Rev.*, 1995, pp. 937–941.
- [97] W. Mickelson, A. Sussman, A. Zettl, W. Mickelson, A. Sussman, and A. Zettl, "Low-power, fast, selective nanoparticle-based hydrogen sulfide gas sensor," *Appl. Phys. Lett.*, vol. 100, p. 173110, 2012.
- [98] W. Shin, K. Tajima, Y. Choi, N. Izu, I. Matsubara, and N. Murayama, "Planar catalytic combustor film for thermoelectric hydrogen sensors," *Sensors Actuators B Chem.*, vol. 108, pp. 455–460, 2005.
- [99] L. Houlet, W. Shin, K. Tajima, M. Nishibori, N. Izu, T. Itoh, and I. Matsubara, "Thermopile sensor-devices for the catalytic detection of hydrogen gas," *Sensors Actuators B Chem.*, vol. 130, no. 1, pp. 200–206, Mar. 2008.
- [100] M. A. Worsley, T. T. Pham, A. Yan, S. J. Shin, J. R. I. Lee, M. Bagge-Hansen, W. Mickelson, and A. Zettl, "Synthesis and characterization of highly crystalline graphene aerogels," *ACS Nano*, vol. 8, no. 10, pp. 11013–22, Oct. 2014.
- [101] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, "Superior Thermal Conductivity of Single-Layer Graphene," *Nano Lett.*, vol. 8, no. 3, pp. 902–907, 2008.

- [102] M. A. Worsley, S. O. Kucheyev, H. E. Mason, M. D. Merrill, B. P. Mayer, J. Lewicki, C. a. Valdez, M. E. Suss, M. Stadermann, P. J. Pauzauskie, J. H. Satcher, J. Biener, and T. F. Baumann, “Mechanically robust 3D graphene macroassembly with high surface area,” *Chem. Commun.*, vol. 48, no. 67, p. 8428, Aug. 2012.
- [103] W. S. Hummers and R. E. Offeman, “Preparation of graphitic oxide,” *J. Am. Chem. Soc.*, vol. 80, p. 1339, 1958.
- [104] S. Brunauer, P. H. Emmett, and E. Teller, “Adsorption of gases in multimolecular layers,” *J. Am. Chem. Soc.*, vol. 60, pp. 309–319, 1938.
- [105] E. P. Barrett, L. G. Joyner, and P. P. Halenda, “The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms,” *J. Am. Chem. Soc.*, vol. 73, no. 1, pp. 373–380, 1951.
- [106] K. Kinoshita, K. Routsis, and J. A. S. Bett, “The thermal decomposition of platinum(II) and (IV) complexes,” *Thermochim. Acta*, vol. 10, no. 1, pp. 109–117, Sep. 1974.
- [107] M. Rousseas, A. P. Goldstein, W. Mickelson, M. A. Worsley, L. Woo, and A. Zettl, “Synthesis of highly crystalline  $sp^2$ -bonded boron nitride aerogels,” *ACS Nano*, vol. 7, no. 10, pp. 8540–6, Oct. 2013.
- [108] C. Dúcsó, M. Ádám, P. Fürjes, M. Hirschfelder, S. Kulinyi, and I. Bársony, “Explosion-proof monitoring of hydrocarbons by mechanically stabilised, integrable calorimetric microsensors,” *Sensors Actuators B Chem.*, vol. 95, no. 1–3, pp. 189–194, Oct. 2003.
- [109] E. E. Karpov, E. F. Karpov, A. Suchkov, S. Mironov, A. Baranov, V. Sleptsov, and L. Calliari, “Energy efficient planar catalytic sensor for methane measurement,” *Sensors Actuators, A Phys.*, vol. 194, pp. 176–180, Feb. 2013.
- [110] A. Harley-Trochimczyk, J. Chang, Q. Zhou, J. Dong, T. Pham, M. a. Worsley, R. Maboudian, A. Zettl, and W. Mickelson, “Catalytic hydrogen sensing using microheated platinum nanoparticle-loaded graphene aerogel,” *Sensors Actuators, B Chem.*, vol. 206, pp. 399–406, Jan. 2015.
- [111] E. Becker, P. A. Carlsson, H. Grönbeck, and M. Skoglundh, “Methane oxidation over alumina supported platinum investigated by time-resolved in situ XANES spectroscopy,” *J. Catal.*, vol. 252, no. 1, pp. 11–17, 2007.
- [112] A. A. Balandin, “Thermal properties of graphene and nanostructured carbon materials,” *Nat. Mater.*, vol. 10, no. 8, pp. 569–81, Aug. 2011.
- [113] “Sintered Alumina,” *NIST Ceramics Webbook*, 2001. [Online]. Available: <http://srdata.nist.gov/CeramicDataPortal/Pds/Scdaos>.
- [114] J. G. Bralla, “Gas, liquified petroleum,” in *Handbook of Manufacturing Processes: How Products, Components and Materials are Made*, Industrial Press, 2007, pp. 677–678.



- [115] J. Speight, "Gas Processing," in *Handbook of Industrial Hydrocarbon Processes*, Elsevier, 2011, pp. 127–162.
- [116] R. . James and J. . Missenden, "The use of propane in domestic refrigerators," *Int. J. Refrig.*, vol. 15, no. 2, pp. 95–100, Jan. 1992.
- [117] M. A. Alsaad and M. A. Hammad, "The application of propane/butane mixture for domestic refrigerators," *Appl. Therm. Eng.*, vol. 18, no. 9–10, pp. 911–918, Sep. 1998.
- [118] D. P. Nolan, "Physical Properties of Hydrocarbons," in *Handbook of Fire and Explosion Protection Engineering: Principles for Oil, Gas, Chemical, and Related*, William Andrew Publishing, 1996, pp. 27–40.
- [119] F. A. Lewis, "The hydrides of palladium and palladium alloys," *Platin. Met. Rev.*, vol. 4, pp. 132–137, 1960.
- [120] N. K. Nag, "A study on the formation of palladium hydride in a carbon-supported palladium catalyst," *J. Phys. Chem. B*, vol. 105, no. 25, pp. 5945–5949, 2001.
- [121] D.-T. T. Phan and G.-S. S. Chung, "A novel nanoporous Pd-graphene hybrid synthesized by a facile and rapid process for hydrogen detection," *Sensors Actuators, B Chem.*, vol. 210, pp. 661–668, 2015.
- [122] Y. T. Pan, X. Yin, K. S. Kwok, and H. Yang, "Higher-order nanostructures of two-dimensional palladium nanosheets for fast hydrogen sensing," *Nano Lett.*, vol. 14, no. 10, pp. 5953–5959, 2014.
- [123] D. Gupta, D. Dutta, M. Kumar, P. B. Barman, C. K. Sarkar, S. Basu, and S. K. Hazra, "A low temperature hydrogen sensor based on palladium nanoparticles," *Sensors Actuators B Chem.*, vol. 196, pp. 215–222, 2014.
- [124] Y. Chen, J. Zou, S. J. Campbell, and G. L. Caer, "Boron nitride nanotubes: Pronounced resistance to oxidation," *Appl. Phys. Lett.*, vol. 84, no. 13, pp. 2430–2432, 2004.
- [125] C. G. Cofer and J. Economy, "Oxidative and hydrolytic stability of boron nitride — A new approach to improving the oxidation resistance of carbonaceous structures," *Carbon N. Y.*, vol. 33, no. 4, pp. 389–395, 1995.
- [126] L. H. Li, J. Cervenka, K. Watanabe, T. Taniguchi, and Y. Chen, "Strong oxidation resistance of atomically thin boron nitride nanosheets," *ACS Nano*, vol. 8, no. 2, pp. 1457–1462, 2014.
- [127] S. Bernard and P. Miele, "Nanostructured and architected boron nitride from boron, nitrogen and hydrogen-containing molecular and polymeric precursors," *Mater. Today*, vol. 17, no. 9, pp. 443–450, 2014.

- [128] I. Jo, M. T. Pettes, J. Kim, K. Watanabe, T. Taniguchi, Z. Yao, and L. Shi, “Thermal Conductivity and Phonon Transport in Suspended Few-Layer Hexagonal Boron Nitride,” *Nano Lett.*, vol. 13, pp. 550–554, 2013.
- [129] M. L. Cohen and A. Zettl, “The physics of boron nitride nanotubes,” *Phys. Today*, pp. 34–38, 2010.
- [130] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, “Boron nitride nanotubes,” *Science (80-. )*, vol. 269, no. 5226, pp. 966–967, 1995.
- [131] D. Golberg, Y. Bando, C. Tang, and C. Zhi, “Boron Nitride Nanotubes,” *Adv. Mater.*, vol. 19, pp. 2413–2432, 2007.
- [132] D. Golberg, Y. Bando, Y. Huang, T. Terao, M. Mitome, C. Tang, and C. Zhi, “Boron nitride nanotubes and nanowires,” *ACS Nano*, vol. 4, no. 6, pp. 2979–2993, 2010.
- [133] G. R. Bhimanapati, D. Kozuch, and J. Robinson, “Large-Scale Synthesis and Functionalization of Hexagonal Boron Nitride Nanosheets,” *Nanoscale*, vol. 6, pp. 11671–11675, 2014.
- [134] L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, and P. M. Ajayan, “Large scale growth and characterization of atomic hexagonal boron nitride layers,” *Nano Lett.*, vol. 10, no. 8, pp. 3209–3215, 2010.
- [135] X. Zeng, L. Ye, S. Yu, R. Sun, J. Xu, and C. P. Wong, “Facile Preparation of Superelastic and Ultralow Dielectric Boron Nitride Nanosheet Aerogels via Freeze-Casting Process,” *Chem. Mater.*, vol. 27, no. 17, pp. 5849–5855, 2015.
- [136] X. Huang, C. Tan, Z. Yin, and H. Zhang, “Hybrid nanostructures based on two-dimensional nanomaterials,” *Adv. Mater.*, vol. 26, no. 14, pp. 2185–204, Apr. 2014.
- [137] T. T. Borek, W. Ackerman, D. W. Hua, R. T. Paine, and D. M. Smith, “Highly microporous boron nitride for gas adsorption,” *Langmuir*, vol. 7, no. 11, pp. 2844–2846, 1991.
- [138] Q. Weng, X. Wang, Y. Bando, and D. Golberg, “One-step template-free synthesis of highly porous boron nitride microsponges for hydrogen storage,” *Adv. Energy Mater.*, vol. 4, p. 1301525, 2014.
- [139] J. Li, J. Lin, X. Xu, X. Zhang, Y. Xue, J. Mi, Z. Mo, Y. Fan, L. Hu, X. Yang, J. Zhang, F. Meng, S. Yuan, and C. Tang, “Porous boron nitride with a high surface area: hydrogen storage and water treatment,” *Nanotechnology*, vol. 24, p. 155603, 2013.
- [140] J. Kim, J. Han, M. Seo, S. Kang, D. Kim, and J. Ihm, “High-surface area ceramic-derived boron-nitride and its hydrogen uptake properties,” *J. Mater. Chem. A*, vol. 1, pp. 1014–1017, 2013.

- [141] W. Lei, D. Portehault, D. Liu, S. Qin, and Y. Chen, "Porous boron nitride nanosheets for effective water cleaning," *Nat. Commun.*, vol. 4, p. 1777, 2013.
- [142] X. Zhang, G. Lian, S. Zhang, D. Cui, and Q. Wang, "Boron nitride nanocarpet: controllable synthesis and their adsorption performance to organic pollutants," *Crystengcomm*, vol. 14, no. 14, pp. 4670–4676, 2012.
- [143] T. Pham, A. P. Goldstein, J. P. Lewicki, S. O. Kucheyev, C. Wang, T. P. Russell, M. a Worsley, L. Woo, W. Mickelson, and A. Zettl, "Nanoscale structure and superhydrophobicity of  $sp^2$ -bonded boron nitride aerogels," *Nanoscale*, vol. 7, no. 23, pp. 10449–58, 2015.
- [144] F. Liu, J. Yu, X. Ji, and M. Qian, "Nanosheet-Structured Boron Nitride Spheres with a Versatile Adsorption Capacity for Water Cleaning," *ACS Appl. Mater. Interfaces*, vol. 7, pp. 1824–1832, 2015.
- [145] S.-H. Jhi and Y.-K. Kwon, "Hydrogen adsorption on boron nitride nanotubes: A path to room-temperature hydrogen storage," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 69, p. 245407, 2004.
- [146] J. A. Perdigón-Melón, A. Auroux, J. M. Guil, and B. Bonnetot, "Preparation of BN catalyst supports from molecular precursors. Influence of the precursor on the properties of the BN ceramic," *Stud. Surf. Sci. Catal.*, vol. 143, pp. 227–237, 2000.
- [147] J. C. S. Wu, C.-Y. Chen, and S. D. Lin, "Boron nitride supported Pt catalyst for selective hydrogenation," *Catal. Letters*, vol. 102, no. 3–4, pp. 223–227, 2005.
- [148] G. Postole, A. Gervasini, A. Auroux, and B. Bonnetot, "Boron Nitride Supported Metal Catalysts: Influence of the Metal and Preparation Method," *Mater. Sci. Forum*, vol. 518, pp. 203–210, 2006.
- [149] Y. Yabe, T. Yamada, S. Nagata, Y. Sawama, Y. Monguchi, and H. Sajiki, "Development of a palladium on boron nitride catalyst and its application to the semihydrogenation of alkynes," *Adv. Synth. Catal.*, vol. 354, no. 7, pp. 1264–1268, 2012.
- [150] N. Meyer, K. Bekaert, D. Pirson, M. Devillers, and S. Hermans, "Boron nitride as an alternative support of Pd catalysts for the selective oxidation of lactose," *Catal. Commun.*, vol. 29, pp. 170–174, 2012.
- [151] M. Zanini, J. H. Visser, L. Rimai, R. E. Soltis, A. Kovalchuk, D. W. Hoffman, E. M. Logothetis, U. Bonne, L. Brewer, O. W. Bynum, and M. A. Richard, "Fabrication and properties of a Si-based high-sensitivity microcalorimetric gas sensor," *Sensors Actuators A Phys.*, vol. 48, no. 3, pp. 187–192, 1995.
- [152] S. M. Jung, H. Y. Jung, M. S. Dresselhaus, Y. J. Jung, and J. Kong, "A facile route for 3D aerogels from nanostructured 1D and 2D materials," *Sci. Rep.*, vol. 2, p. 849, Jan. 2012.

- [153] A. Monshi, M. R. Foroughi, and M. R. Monshi, "Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD," *World J. Nano Sci. Eng.*, vol. 2, pp. 154–160, 2012.
- [154] C.-A. Lin, J. C. S. Wu, J.-W. Pan, and C.-T. Yeh, "Characterization of Boron-Nitride-Supported Pt Catalysts for the Deep Oxidation of Benzene," *J. Catal.*, vol. 210, pp. 39–45, 2002.
- [155] "VQ548MP Datasheet," *SGX Sensortech*, 2014. .
- [156] A. Chiba, M. Komoda, T. Kosumi, T. Nanba, N. Azuma, and A. Ueno, "Difference in catalytic combustion of propane and propene on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst," *Chem. Lett.*, vol. 28, no. 8, pp. 801–802, 1999.
- [157] K. Bijjula, "Gaseous Reactive Flows Around Catalytically Combusting Micro-Wires," 2008.
- [158] J. C.-S. Wu, Z.-A. Lin, J.-W. Pan, and M.-H. Rei, "A novel boron nitride supported Pt catalyst for VOC incineration," *Appl. Catal. A Gen.*, vol. 219, no. 1–2, pp. 117–124, 2001.
- [159] O. Grudin, R. Marinescu, L. Landsberger, D. Cheeke, and M. Kahrizi, "Microstructure release and test techniques for high-temperature micro hotplate," in *Proceedings of the 1999 IEEE Canadian Conference on Electrical and Computer Engineering*, 1999, pp. 1610–1615.
- [160] O. Paul and P. Ruther, "Testing the limits of silicon technology based MEMS materials," *Proc. 2003 Int. Symp. Micromechatronics Hum. Sci.*, pp. 1–9, 2003.
- [161] R. Maboudian, C. Carraro, D. G. Senesky, and C. S. Roper, "Advances in silicon carbide science and technology at the micro- and nanoscales," *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 31, no. 5, p. 050805, 2013.
- [162] L. Chen and M. Mehregany, "An Examination of Material-Related Performance in SiC Heated Elements for IR Emitter and Sensor Applications," *Mater. Sci. Forum*, vol. 600–603, no. 13, pp. 863–866, 2009.
- [163] G. S. Chung and J. M. Jeong, "Fabrication of micro heaters on polycrystalline 3C-SiC suspended membranes for gas sensors and their characteristics," *Microelectron. Eng.*, vol. 87, no. 11, pp. 2348–2352, 2010.
- [164] F. Solzbacher, C. Imawan, H. Steffes, E. Obermeier, and H. Moller, "A modular system of SiC-based microhotplates for the application in metal oxide gas sensors," *Sensors Actuators B. Chem.*, vol. 64, pp. 95–101, 2000.
- [165] F. Solzbacher, C. Imawan, H. Steffes, E. Obermeier, and M. Eickhoff, "A highly stable SiC based microhotplate NO<sub>2</sub> gas-sensor," *Sensors Actuators, B Chem.*, vol. 78, no. 1–3, pp. 216–220, 2001.

- [166] G. Saxena and R. Paily, "Performance improvement of square microhotplate with insulation layer and heater geometry," *Microsyst. Technol.*, vol. 21, no. 11, pp. 2331–2338, 2014.
- [167] G. Wiche, A. Berns, H. Steffes, and E. Obermeier, "Thermal analysis of silicon carbide based micro hotplates for metal oxide gas sensors," *Sensors Actuators A Phys.*, vol. 123–124, pp. 12–17, Sep. 2005.
- [168] A. V. Korlyakov and V. V. Luchinin, "Silicon Carbide Microheater," in *The 4th International High Temperature Electronics Conference*, 1998, pp. 322–323.
- [169] G. S. Chung and J. M. Jeong, "Fabrication and Characteristics of Micro Heaters Based on Polycrystalline 3C-SiC for High Temperature and Voltage," *Mater. Sci. Forum*, vol. 645–648, pp. 1085–1088, Apr. 2010.
- [170] B. Morana, F. Santagata, L. Mele, M. Mihailović, G. Pandraud, J. F. Creemer, and P. M. Sarro, "A silicon carbide MEMS microhotplate for nanomaterial characterization in tem," *Proc. IEEE Int. Conf. Micro Electro Mech. Syst.*, pp. 380–383, 2011.
- [171] S.-S. Noh, J.-H. Seo, and E.-A. Lee, "The Fabrication by using Surface MEMS of 3C-SiC Micro-heaters and RTD Sensors and their Resultant Properties," *Trans. Electr. Electron. Mater.*, vol. 10, no. 4, pp. 131–134, Aug. 2009.
- [172] G. Rebeiz, "Appendix B: Mechanical, electrical, and thermal properties of RF MEMS materials," in *RF MEMS: Theory, Design, and Technology*, John Wiley & Sons, 2003, pp. 473–478.
- [173] J. Puigcorbe, D. Vogel, B. Michel, A. Vila, I. Gracia, C. Cane, and J. R. Morante, "Thermal and mechanical analysis of micromachined gas sensors," *J. Micromechanics Microengineering*, vol. 13, pp. 548–556, 2003.
- [174] F. Liu, C. Carraro, A. P. Pisano, and R. Maboudian, "Growth and characterization of nitrogen-doped polycrystalline 3C-SiC thin films for harsh environment MEMS applications," *J. Micromechanics Microengineering*, vol. 20, no. 3, p. 035011, 2010.
- [175] D. Gao, R. T. Howe, and R. Maboudian, "High-selectivity etching of polycrystalline 3C-SiC films using HBr-based transformer coupled plasma," *Appl. Phys. Lett.*, vol. 82, no. 11, p. 1742, Mar. 2003.
- [176] A. Harley-Trochimczyk, T. Pham, J. Chang, E. Chen, M. A. Worsley, A. Zettl, W. Mickelson, and R. Maboudian, "Platinum Nanoparticle Loading of Boron Nitride Aerogel and Its Use as a Novel Material for Low-Power Catalytic Gas Sensing," *Adv. Funct. Mater.*, pp. 433–439, 2015.
- [177] J. Zhang, C. Carraro, R. T. Howe, and R. Maboudian, "Electrical, mechanical and metal contact properties of polycrystalline 3C-SiC films for MEMS in harsh environments," *Surf. Coatings Technol.*, vol. 201, no. 22–23 SPEC. ISS., pp. 8893–8898, 2007.

- [178] A. Harley-Trochimczyk, J. Chang, T. Pham, J. Dong, M. A. Worsley, A. Zettl, W. Mickelson, and R. Maboudian, "Low power microheater-based combustible gas sensor with graphene aerogel catalyst support," in *Technical Digest of the 18th International Conference on Solid-State Sensors, Actuators, and Microsystems (Tranducers '15)*, 2015, pp. 1483–1486.
- [179] M. Engel, M. Baumbach, T. Kammerer, and A. Schutze, "Preparation of Microstructured Pellistors and their Application for Fast Fuel Vapor Discrimination," *IEEE*, pp. 268–271, 2004.
- [180] X. Huang, F. Meng, Z. Pi, W. Xu, and J. Liu, "Gas sensing behavior of a single tin dioxide sensor under dynamic temperature modulation," *Sensors Actuators, B Chem.*, vol. 99, no. 2–3, pp. 444–450, 2004.
- [181] A. Gramm and A. Schutze, "High performance solvent vapor identification with a two sensor array using temperature cycling and pattern classification," *Sensors Actuators, B Chem.*, vol. 95, pp. 58–65, 2003.
- [182] K. S. Novoselov, A. K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, I. V Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films.," *Science (80-. )*, vol. 306, pp. 666–9, Oct. 2004.
- [183] T. O. Wehling, K. S. Novoselov, S. V Morozov, E. E. Vdovin, M. I. Katsnelson, A. K. Geim, and A. I. Lichtenstein, "Molecular doping of graphene," *Nano Lett.*, vol. 8, no. 1, pp. 173–7, Jan. 2008.
- [184] Y. Yao, L. Tolentino, Z. Yang, X. Song, W. Zhang, Y. Chen, and C. Wong, "High-Concentration Aqueous Dispersions of MoS<sub>2</sub>," *Adv. Funct. Mater.*, vol. 23, no. 28, pp. 3577–3583, Jul. 2013.
- [185] F. K. Perkins, A. L. Friedman, E. Cobas, P. M. Campbell, G. G. Jernigan, and B. T. Jonker, "Chemical vapor sensing with monolayer MoS<sub>2</sub>," *Nano Lett.*, vol. 13, no. 2, pp. 668–73, Feb. 2013.
- [186] B. Cho, A. R. Kim, Y. Park, J. Yoon, Y.-J. Lee, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, H. C. Ko, D.-H. Kim, and M. G. Hahm, "Bifunctional sensing characteristics of chemical vapor deposition synthesized atomic-layered MoS<sub>2</sub>," *ACS Appl. Mater. Interfaces*, vol. 7, no. 4, pp. 2952–9, Feb. 2015.
- [187] B. Cho, M. G. Hahm, M. Choi, J. Yoon, A. R. Kim, Y.-J. Lee, S.-G. Park, J.-D. Kwon, C. S. Kim, M. Song, Y. Jeong, K.-S. Nam, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, H. C. Ko, P. M. Ajayan, and D.-H. Kim, "Charge-transfer-based gas sensing using atomic-layer MoS<sub>2</sub>," *Sci. Rep.*, vol. 5, p. 8052, Jan. 2015.
- [188] J.-S. Kim, H.-W. Yoo, H. O. Choi, and H.-T. Jung, "Tunable volatile organic compounds sensor by using thiolated ligand conjugation on MoS<sub>2</sub>," *Nano Lett.*, vol. 14, no. 10, pp. 5941–7, Oct. 2014.

- [189] H. Long, A. Harley-Trochimczyk, T. He, T. Pham, Z. Tang, T. Shi, A. Zettl, W. Mickelson, C. Carraro, and R. Maboudian, "In Situ Localized Growth of Porous Tin Oxide Films on Low Power Microheater Platform for Low Temperature CO Detection," *ACS Sensors*, vol. 1, no. 4, pp. 339–343, 2016.
- [190] M. A. Worsley, P. J. Pauzauskie, T. Y. Olson, J. Biener, J. H. Satcher Jr., and T. F. Baumann, "Synthesis of graphene aerogel with high electrical conductivity," *J. Am. Chem. Soc.*, vol. 132, pp. 14067–14069, Oct. 2010.
- [191] "Nitrogen Dioxide," *United States Environmental Protection Agency*. [Online]. Available: <https://www3.epa.gov/airquality/nitrogenoxides/>. [Accessed: 01-Feb-2015].
- [192] "Carbon Monoxide's Impact on Indoor Air Quality," *United States Environmental Protection Agency*. .
- [193] A. K. Geim, "Graphene: Status and prospects," *Science (80-. )*, vol. 324, pp. 1–8, 2009.
- [194] J. D. Fowler, M. J. Allen, V. C. Tung, Y. Yang, R. B. Kaner, and B. H. Weiller, "Practical chemical sensors from chemically derived graphene.," *ACS Nano*, vol. 3, no. 2, pp. 301–6, Feb. 2009.
- [195] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, "Single-layer MoS<sub>2</sub> transistors," *Nat. Nanotechnol.*, vol. 6, no. 3, pp. 147–50, Mar. 2011.
- [196] M. A. Worsley, S. J. Shin, M. D. Merrill, J. Lenhardt, A. J. Nelson, L. Y. Woo, A. E. Gash, T. F. Baumann, and C. A. Orme, "Ultralow Density, Monolithic WS<sub>2</sub>, MoS<sub>2</sub>, and MoS<sub>2</sub>/Graphene Aerogels," *ACS Nano*, vol. 9, no. 5, pp. 4698–4705, 2015.
- [197] K. Roy, M. Padmanabhan, S. Goswami, T. P. Sai, G. Ramalingam, S. Raghavan, and A. Ghosh, "Graphene-MoS<sub>2</sub> hybrid structures for multifunctional photoresponsive memory devices," *Nat. Nanotechnol.*, vol. 8, no. 11, pp. 826–30, Nov. 2013.
- [198] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, and H. Dai, "MoS<sub>2</sub> nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction," *J. Am. Chem. Soc.*, vol. 133, no. 19, pp. 7296–9, May 2011.
- [199] R. Yan, J. R. Simpson, S. Bertolazzi, J. Brivio, M. Watson, X. Wu, A. Kis, T. Luo, A. R. Hight Walker, and H. G. Xing, "Thermal conductivity of monolayer molybdenum disulfide obtained from temperature-dependent Raman spectroscopy," *ACS Nano*, vol. 8, no. 1, pp. 986–93, Jan. 2014.
- [200] Y. Hou, B. Zhang, Z. Wen, S. Cui, X. Guo, Z. He, and J. Chen, "A 3D hybrid of layered MoS<sub>2</sub>/nitrogen-doped graphene nanosheet aerogels: an effective catalyst for hydrogen evolution in microbial electrolysis cells," *J. Mater. Chem. A*, vol. 2, no. 34, p. 13795, Jun. 2014.



- [201] Y. Zhao, X. Xie, J. Zhang, H. Liu, H.-J. Ahn, K. Sun, and G. Wang, "MoS<sub>2</sub> Nanosheets Supported on 3D Graphene Aerogel as a Highly Efficient Catalyst for Hydrogen Evolution," *Chemistry (Easton)*, vol. 21, no. 45, pp. 15908–13, Nov. 2015.
- [202] K. Chang, Z. Mei, T. Wang, Q. Kang, S. Ouyang, and J. Ye, "MoS<sub>2</sub>/graphene cocatalyst for efficient photocatalytic H<sub>2</sub> evolution under visible light irradiation," *ACS Nano*, vol. 8, no. 7, pp. 7078–87, Jul. 2014.
- [203] K.-J. Huang, L. Wang, J.-Z. Zhang, and K. Xing, "Synthesis of molybdenum disulfide/carbon aerogel composites for supercapacitors electrode material application," *J. Electroanal. Chem.*, vol. 752, pp. 33–40, Sep. 2015.
- [204] K. Chang and W. Chen, "L-cysteine-assisted synthesis of layered MoS<sub>2</sub>/graphene composites with excellent electrochemical performances for lithium ion batteries," *ACS Nano*, vol. 5, no. 6, pp. 4720–8, Jun. 2011.
- [205] P. T. K. Loan, W. Zhang, C.-T. Lin, K.-H. Wei, L.-J. Li, and C.-H. Chen, "Graphene/MoS<sub>2</sub> heterostructures for ultrasensitive detection of DNA hybridisation," *Adv. Mater.*, vol. 26, no. 28, pp. 4838–44, Jul. 2014.
- [206] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, "Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition," *Nano Lett.*, vol. 9, no. 1, pp. 30–5, Jan. 2009.
- [207] A. Azcatl, S. McDonnell, S. K. C., X. Peng, H. Dong, X. Qin, R. Addou, G. I. Mordi, N. Lu, J. Kim, M. J. Kim, K. Cho, and R. M. Wallace, "MoS<sub>2</sub> functionalization for ultra-thin atomic layer deposited dielectrics," *Appl. Phys. Lett.*, vol. 104, no. 11, p. 111601, Mar. 2014.
- [208] H. Nan, Z. Wang, W. Wang, Z. Liang, Y. Lu, Q. Chen, D. He, P. Tan, F. Miao, X. Wang, J. Wang, and Z. Ni, "Strong photoluminescence enhancement of MoS<sub>2</sub> through defect engineering and oxygen bonding," *ACS Nano*, vol. 8, no. 6, pp. 5738–45, Jun. 2014.
- [209] E. G. da Silveira Firmiano, A. C. Rabelo, C. J. Dalmaschio, A. N. Pinheiro, E. C. Pereira, W. H. Schreiner, and E. R. Leite, "Supercapacitor Electrodes Obtained by Directly Bonding 2D MoS<sub>2</sub> on Reduced Graphene Oxide," *Adv. Energy Mater.*, vol. 4, no. 6, p. 1301380, Apr. 2014.
- [210] L. Li, S. He, M. Liu, C. Zhang, and W. Chen, "Three-Dimensional Mesoporous Graphene Aerogel-Supported SnO<sub>2</sub> Nanocrystals for High-Performance NO<sub>2</sub> Gas Sensing at Low Temperature," *Anal. Chem.*, vol. 87, no. 3, pp. 1638–1645, 2015.
- [211] X. Liu, J. Cui, J. Sun, and X. Zhang, "3D graphene aerogel-supported SnO<sub>2</sub> nanoparticles for efficient detection of NO<sub>2</sub>," *RSC Adv.*, vol. 4, no. 43, p. 22601, 2014.

- [212] X. Liu, J. Sun, and X. Zhang, "Novel 3D graphene aerogel-ZnO composites as efficient detection for NO<sub>2</sub> at room temperature," *Sensors Actuators, B Chem.*, vol. 211, pp. 220–226, 2015.
- [213] D. T. Phan and G. S. Chung, "P-n junction characteristics of graphene oxide and reduced graphene oxide on n-type Si(111)," *J. Phys. Chem. Solids*, vol. 74, no. 11, pp. 1509–1514, 2013.
- [214] I. Iezhokin, P. Offermans, S. H. Brongersma, A. J. M. Giesbers, and C. F. J. Flipse, "High sensitive quasi freestanding epitaxial graphene gas sensor on 6H-SiC," *Appl. Phys. Lett.*, vol. 103, no. 5, 2013.
- [215] G. Lu, L. E. Ocola, and J. Chen, "Gas detection using low-temperature reduced graphene oxide sheets," *Appl. Phys. Lett.*, vol. 94, no. 8, pp. 2007–2010, Feb. 2009.
- [216] A. Lipatov, A. Varezchnikov, M. Augustin, M. Bruns, M. Sommer, V. Sysoev, A. Kolmakov, and A. Sinitskii, "Intrinsic device-to-device variation in graphene field-effect transistors on a Si/SiO<sub>2</sub> substrate as a platform for discriminative gas sensing," *Appl. Phys. Lett.*, vol. 104, no. 1, 2014.
- [217] Y. Liu, S. Lin, and L. Lin, "A versatile gas sensor with selectivity using a single graphene transistor," in *Technical Digest of the 18th International Conference on Solid-State Sensors, Actuators, and Microsystems (Tranducers '15)*, 2015, pp. 961–964.
- [218] S. Rumyantsev, G. Liu, M. Shur, R. A. Potyrailo, and A. A. Balandin, "Selective Gas Sensing with a Single Graphene Pristine Transistor," *Nano Lett.*, pp. 1–17, 2012.
- [219] L. Boon-Brett, J. Bousek, and P. Moretto, "Reliability of commercially available hydrogen sensors for detection of hydrogen at critical concentrations: Part II - selected sensor test results," *Int. J. Hydrogen Energy*, vol. 34, pp. 562–571, 2009.
- [220] "Technical Note TN-121: CO Sensor Cross-Sensitivity And Removal With A Charcoal Filter." RAE Systems, pp. 1–2, 2000.
- [221] J. Kong, N. Franklin, C. Zhou, M. Chapline, S. Peng, K. Cho, and H. Dai, "Nanotube molecular wires as chemical sensors," *Science (80-. )*, vol. 287, no. 5453, pp. 622–5, Jan. 2000.
- [222] J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei, and P. E. Sheehan, "Reduced graphene oxide molecular sensors," *Nano Lett.*, vol. 8, no. 10, pp. 3137–40, Oct. 2008.
- [223] H. Choi, J. S. Choi, J.-S. Kim, J.-H. Choe, K. H. Chung, J.-W. Shin, J. T. Kim, D.-H. Youn, K.-C. Kim, J.-I. Lee, S.-Y. Choi, P. Kim, C.-G. Choi, and Y.-J. Yu, "Flexible and transparent gas molecule sensor integrated with sensing and heating graphene layers," *Small*, vol. 10, no. 18, pp. 3685–91, Sep. 2014.

- [224] R. Samnakay, C. Jiang, S. L. Rumyantsev, M. S. Shur, and A. A. Balandin, "Selective chemical vapor sensing with few-layer MoS<sub>2</sub> thin-film transistors: Comparison with graphene devices," *Appl. Phys. Lett.*, vol. 106, no. 2, pp. 3–8, 2015.
- [225] Q. Yue, Z. Shao, S. Chang, and J. Li, "Adsorption of gas molecules on monolayer MoS<sub>2</sub> and effect of applied electric field," *Nanoscale Res. Lett.*, vol. 8, no. 1, p. 425, Jan. 2013.
- [226] K. Chan, C. Tsai, H. A. Hansen, and J. K. Nørskov, "Molybdenum Sulfides and Selenides as Possible Electrocatalysts for CO<sub>2</sub> Reduction," *ChemCatChem*, vol. 6, no. 7, pp. 1899–1905, Jul. 2014.
- [227] N. Yamazoe and N. Miura, "Environmental gas sensing," *Sensors Actuators B Chem.*, vol. 20, no. 2–3, pp. 95–102, Jun. 1994.
- [228] F. Röck, N. Barsan, and U. Weimar, "Electronic nose: current status and future trends," *Chem. Rev.*, vol. 108, no. 2, pp. 705–25, Feb. 2008.
- [229] M. I. Mead, O. A. M. Popoola, G. B. Stewart, P. Landshoff, M. Calleja, M. Hayes, J. J. Baldovi, M. W. McLeod, T. F. Hodgson, J. Dicks, A. Lewis, J. Cohen, R. Baron, J. R. Saffell, and R. L. Jones, "The use of electrochemical sensors for monitoring urban air quality in low-cost, high-density networks," *Atmos. Environ.*, vol. 70, pp. 186–203, May 2013.
- [230] G. Sberveglieri, "Recent developments in semiconducting thin-film gas sensors," *Sensors Actuators B Chem.*, vol. 23, no. 2–3, pp. 103–109, Feb. 1995.
- [231] T. Becker, S. Mühlberger, C. B. Braunmühl, G. Müller, T. Ziemann, and K. Hechtenberg, "Air pollution monitoring using tin-oxide-based microreactor systems," *Sensors Actuators B Chem.*, vol. 69, no. 1–2, pp. 108–119, Sep. 2000.
- [232] G. Korotcenkov, "Metal oxides for solid-state gas sensors: What determines our choice?," *Mater. Sci. Eng. B*, vol. 139, no. 1, pp. 1–23, Apr. 2007.
- [233] M. E. Franke, T. J. Koplin, and U. Simon, "Metal and metal oxide nanoparticles in chemiresistors: does the nanoscale matter?," *Small*, vol. 2, no. 1, pp. 36–50, Jan. 2006.
- [234] M. Hübner, D. Koziej, M. Bauer, N. Barsan, K. Kvashnina, M. D. Rossell, U. Weimar, and J.-D. Grunwaldt, "The structure and behavior of platinum in SnO<sub>2</sub>-based sensors under working conditions," *Angew. Chem. Int. Ed. Engl.*, vol. 50, no. 12, pp. 2841–4, Mar. 2011.
- [235] U. Dibbern, "A substrate for thin-film gas sensors in microelectronic technology," *Sensors Actuators B Chem.*, vol. 2, no. 1, pp. 63–70, Mar. 1990.
- [236] S. E. Moon, H.-K. Lee, N.-J. Choi, J. Lee, C. A. Choi, W. S. Yang, J. Kim, J. J. Jong, and D.-J. Yoo, "Low power consumption micro C<sub>2</sub>H<sub>5</sub>OH gas sensor based on micro-heater and screen printing technique," *Sensors Actuators B Chem.*, vol. 187, pp. 598–603, Oct. 2013.

- [237] Z. Dai, L. Xu, G. Duan, T. Li, H. Zhang, Y. Li, Y. Wang, Y. Wang, and W. Cai, "Fast-response, sensitive and low-powered chemosensors by fusing nanostructured porous thin film and IDEs-microheater chip," *Sci. Rep.*, vol. 3, p. 1669, Jan. 2013.
- [238] F. Sun, W. Cai, Y. Li, L. Jia, and F. Lu, "Direct Growth of Mono- and Multilayer Nanostructured Porous Films on Curved Surfaces and Their Application as Gas Sensors," *Adv. Mater.*, vol. 17, no. 23, pp. 2872–2877, Dec. 2005.
- [239] J. Zhang, J. Guo, H. Xu, and B. Cao, "Reactive-template fabrication of porous SnO<sub>2</sub> nanotubes and their remarkable gas-sensing performance," *ACS Appl. Mater. Interfaces*, vol. 5, no. 16, pp. 7893–8, Aug. 2013.
- [240] Y. Jia, L. He, Z. Guo, X. Chen, F. Meng, T. Luo, M. Li, and J. Liu, "Preparation of Porous Tin Oxide Nanotubes Using Carbon Nanotubes as Templates and Their Gas-Sensing Properties," *J. Phys. Chem. C*, vol. 113, no. 22, pp. 9581–9587, Jun. 2009.
- [241] A. Kolmakov, Y. Zhang, G. Cheng, and M. Moskovits, "Detection of CO and O<sub>2</sub> Using Tin Oxide Nanowire Sensors," *Adv. Mater.*, vol. 15, no. 12, pp. 997–1000, Jun. 2003.
- [242] J. Jang, R. Kitsomboonloha, S. L. Swisher, E. S. Park, H. Kang, and V. Subramanian, "Transparent high-performance thin film transistors from solution-processed SnO<sub>2</sub>/ZrO<sub>2</sub> gel-like precursors," *Adv. Mater.*, vol. 25, no. 7, pp. 1042–7, Feb. 2013.
- [243] U. Ünal and G. Somer, "Simultaneous determination of trace Sn(II) and Sn(IV) using differential pulse polarography and application," *Turkish J. Chem.*, vol. 35, no. 1, pp. 73–85, Jan. 2011.
- [244] Q. Cao, K.-C. Xie, Y.-K. Lv, and W.-R. Bao, "Process effects on activated carbon with large specific surface area from corn cob," *Bioresour. Technol.*, vol. 97, no. 1, pp. 110–5, Jan. 2006.
- [245] M. Guerrero, M. P. Ruiz, M. U. Alzueta, R. Bilbao, and A. Millera, "Pyrolysis of eucalyptus at different heating rates: studies of char characterization and oxidative reactivity," *J. Anal. Appl. Pyrolysis*, vol. 74, no. 1–2, pp. 307–314, Aug. 2005.
- [246] D. G. Roberts, D. J. Harris, and T. F. Wall, "On the Effects of High Pressure and Heating Rate during Coal Pyrolysis on Char Gasification Reactivity," *Energy & Fuels*, vol. 17, no. 4, pp. 887–895, Jul. 2003.
- [247] S. Ghosh, M. Narjinary, A. Sen, R. Bandyopadhyay, and S. Roy, "Fast detection of low concentration carbon monoxide using calcium-loaded tin oxide sensors," *Sensors Actuators B Chem.*, vol. 203, pp. 490–496, Nov. 2014.
- [248] C. J. Martinez, B. Hockey, C. B. Montgomery, and S. Semancik, "Porous tin oxide nanostructured microspheres for sensor applications," *Langmuir*, vol. 21, no. 17, pp. 7937–44, Aug. 2005.

- [249] L. Zhang and Y. Yin, "Hierarchically mesoporous SnO<sub>2</sub> nanosheets: Hydrothermal synthesis and highly ethanol-sensitive properties operated at low temperature," *Sensors Actuators B Chem.*, vol. 185, pp. 594–601, Aug. 2013.
- [250] Y.-F. Sun, S.-B. Liu, F.-L. Meng, J.-Y. Liu, Z. Jin, L.-T. Kong, and J.-H. Liu, "Metal Oxide Nanostructures and Their Gas Sensing Properties: A Review," *Sensors*, vol. 12, no. 3, pp. 2610–2631, 2012.
- [251] Q. Yan and X. Liu, "Non-heating room temperature SnO<sub>2</sub> gas sensors," *Electrochem. Soc. Proc.*, vol. 8, pp. 158–164, 2004.
- [252] M. A. Andio, P. N. Browning, P. A. Morris, and S. A. Akbar, "Comparison of gas sensor performance of SnO<sub>2</sub> nano-structures on microhotplate platforms," *Sensors Actuators B Chem.*, vol. 165, no. 1, pp. 13–18, Apr. 2012.
- [253] S. Shukla, S. Seal, L. Ludwig, and C. Parish, "Nanocrystalline indium oxide-doped tin oxide thin film as low temperature hydrogen sensor," *Sensors Actuators B Chem.*, vol. 97, no. 2–3, pp. 256–265, Feb. 2004.
- [254] H. Huang, Y. C. Lee, O. K. Tan, W. Zhou, N. Peng, and Q. Zhang, "High sensitivity SnO<sub>2</sub> single-nanorod sensors for the detection of H<sub>2</sub> gas at low temperature.," *Nanotechnology*, vol. 20, no. 11, p. 115501, Mar. 2009.
- [255] R. Ab Kadir, Z. Li, A. Z. Sadek, R. Abdul Rani, A. S. Zoolfakar, M. R. Field, J. Z. Ou, A. F. Chrimes, and K. Kalantar-zadeh, "Electrospun Granular Hollow SnO<sub>2</sub> Nanofibers Hydrogen Gas Sensors Operating at Low Temperatures," *J. Phys. Chem. C*, vol. 118, no. 6, pp. 3129–3139, Feb. 2014.
- [256] N. Yamazoe and K. Shimano, "Roles of Shape and Size of Component Crystals in Semiconductor Gas Sensors," *J. Electrochem. Soc.*, vol. 155, no. 4, p. J85, Apr. 2008.
- [257] L. Xu, T. Li, X. Gao, and Y. Wang, "Behaviour of a Catalytic Combustion Methane Gas Sensor Working on Pulse Mode," *IEEE Sens. J.*, pp. 391–394, 2010.
- [258] Q. Chen, H. Dong, and S. Xia, "A novel micro-pellistor based on nanoporous alumina beam support," *J. Electron.*, vol. 29, no. 5, pp. 469–472, Aug. 2012.
- [259] J. H. Lee and D. L. Trimm, "Catalytic Combustion of Methane," *Fuel Process. Technol.*, vol. 42, no. 2–3, pp. 339–359, 1995.
- [260] M. Niwa, K. Awano, and Y. Murakami, "Activity of supported platinum catalysts for methane oxidation," *Appl. Catal.*, vol. 7, no. 3, pp. 317–325, 1983.
- [261] C. F. Cullis and B. M. Willatt, "Oxidation of Methane over Supported Precious Metal Catalysts," *J. Catal.*, vol. 83, pp. 267–285, 1983.

- [262] A. Ishikawa, S. Komai, A. Satsuma, T. Hattori, and Y. Murakami, "Solid superacid as the support of a platinum catalyst for low-temperature catalytic combustion," *Appl. Catal. A Gen.*, vol. 110, no. 1, pp. 61–66, 1994.
- [263] J. C. S. Wu and S. J. Lin, "Novel BN supported bi-metal catalyst for oxydehydrogenation of propane," *Chem. Eng. J.*, vol. 140, no. 1–3, pp. 391–397, 2008.
- [264] T. F. Garetto, E. Rincón, and C. R. Apesteguía, "Deep oxidation of propane on Pt-supported catalysts: Drastic turnover rate enhancement using zeolite supports," *Appl. Catal. B Environ.*, vol. 48, no. 3, pp. 167–174, 2004.