Investigation into the hydrogen gas sensing mechanism of 3C-SiC resistive gas sensors

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University of South Florida

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Investigation into the Hydrogen Gas Sensing Mechanism of 3C-SiC Resistive Gas Sensors

by

Timothy J. Fawcett

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
Department of Chemical Engineering
College of Engineering
University of South Florida

Major Professor: John T. Wolan, Ph.D.
Stephen E. Saddow, Ph.D.
Andrew M. Hoff, Ph.D.
Norma A. Alcantar, Ph.D.
David A. Rabson, Ph.D.
Anita Lloyd Spetz, Ph.D.

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Keywords: cubic silicon carbide, thermal detection, thermal conductivity, heat transfer, silicon-on-insulator

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Dedication

I would like to dedicate this dissertation to my family, especially my wife for supporting me for these past few years. Without all of you, I would not be in the position I am today. Thank you.
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Investigation into the Hydrogen Gas Sensing Mechanism of 3C-SiC Resistive Gas Sensors

Timothy J. Fawcett

ABSTRACT

The hydrogen (H\textsubscript{2}) gas sensing mechanism driving 3C-SiC resistive gas sensors is investigated in this work in which two hypotheses are proposed. One hypothesis involves the surface adsorption of H\textsubscript{2} on the sensor surface with the adsorbed molecules influencing the flow of current in a resistive gas sensor, termed the surface adsorption detection mechanism. The second hypothesis includes the transfer of heat from the sensor to the gas, producing a change in the temperature of the device when the heat transfer characteristics of the gas change, termed the thermal detection mechanism. The heat transfer characteristics of the gas are dependent on the thermal conductivity of the gas, a property which is a strong function of gas composition. Thus, the thermal detection mechanism mainly detects changes in the thermal conductivity of a gas or gas mixture.

Initial experiments suggested the surface adsorption mechanism as the detection mechanism of resistive 3C-SiC gas sensors. However, these experiments were performed in the absence of device temperature measurements. Recent experiments in which the device temperature was measured with a resistance temperature detector (RTD) in thermal contact with the device strongly support the thermal detection mechanism as being responsible for hydrogen gas detection. Experimental observations show the temperature of the resistive 3C-SiC hydrogen gas sensors changes greatly with changing hydrogen gas composition. For example, a 3C-SiC/SOI resistive sensor biased at 10 Vdc displayed a change in temperature from \(~400^\circ\text{C}\) to \(~216^\circ\text{C}\), correlating to a change in current from \(~41\ mA\) to \(~6\ mA\), upon the introduction of 100\% H\textsubscript{2}. The this 3C-SiC/SOI resistive sensor, this large decrease in temperature caused a large increase in resistance which is detected as a decrease in current. Several different experiments have also been performed to confirm the thermal detection mechanism hypothesis.
Chapter 1:  Introduction

1.1 Gas sensor overview

Advancing technology has driven the development of gas sensors able to operate at high temperatures and in harsh environments. Gas sensors are needed to monitor fuel cell [1,2] and automotive exhaust emissions [3], air pollution [4,5], chemical processes [6], and flue gas compositions [7] for safety and process control. Many material systems have been investigated for use as gas sensors with the most successful being semiconductors [8-10] and semiconducting metal oxides [11,12]. For operation at high temperatures (> 200°C), wide bandgap semiconductor materials are generally required [13] with silicon carbide (SiC) being one of the most studied material systems for high temperature harsh environment gas sensing [3,6-9,14-25].

Many different device structures have been studied for gas sensing applications. These device structures range from surface acoustic wave (SAW) devices built on piezoelectric materials [26] to semiconductor based devices including metal-semiconductor (MS) [14,19] and metal-oxide-semiconductor (MOS) devices [3,10,23,27]. Thermal conductivity sensors fabricated from a wide variety of materials, ranging from Si to Pt have also been developed [28-33]. This study focuses on the use of resistive MS devices for the detection of hydrogen (H₂). Semiconductor and thermal conductivity based gas sensing devices are described below.

1.1.1 Semiconductor based gas sensor device structures

Several different semiconductor device structures have been employed as gas sensors including Schottky barrier diode [9,19-21], MOS capacitor [34], MOS field-effect transistor (MOSFET) [3,7,25,27,35], and resistive [14,36] structures. All of these device structures, except resistive devices, employ a catalytic metal gate to aid in gas detection. The metal contacts for resistive structures do not necessarily need catalytic properties. A brief overview of the structure and operation of these device structures is given below.

1.1.1.1 Catalytic metal gate devices

Several gas sensing device structures employ the use of a catalytic metal gate to assist in the detection of specific gases. Schottky barrier diode, MOS capacitors and MOSFETs have all been used in conjunction with different catalytic metal gates, usually Pt, Pd, Ru, or Ir, to detect specific gases [23]. Schematics of these device structures are presented in Figure 1.1. The catalytic metal gate, sometimes referred to as top-side contact, reacts with the detection gas, producing a response that can be measured electrically. For example, the detection of hydrogen containing species is routinely performed using catalytic metal gate devices. The hydrogen containing species dissociates on the catalytic metal surface forming atomic hydrogen (H) [37]. These H atoms then diffuse to the metal-insulator interface and form a dipole layer which changes the electrical properties
of the device [10,23,27]. For example, this dipole layer shifts the current vs. voltage (I-V) characteristics for a Schottky diode sensor, as shown in Figure 1.2 [24,38].

Figure 1.1. Catalytic metal gate gas sensing device structures [23].

Figure 1.2. Shift in I-V characteristics in a Schottky diode sensor [24].

1.1.1.2 Resistive gas sensors

Resistive gas sensors can be categorized by the substrate material from which they are built. Semiconducting metal-oxides [11,12,39] were the first resistive gas sensors while wide bandgap materials have recently attracted much interest [14,40]. Although the device structure for both material systems is similar, as shown in Figure 1.3, their detection mechanisms are very different. Semiconducting metal-oxide resistive sensors detect gaseous species by induced changes in the stoichiometry of the metal-oxide surface upon reaction with the target species. These changes in stoichiometry give rise to a change in the resistance of the device, which is interpreted as the sensor response.
[36,41]. The detection mechanism behind wide bandgap metal-semiconductor resistive sensors is the topic of this dissertation, and will be explored below.

![Diagram of a general resistive sensor device structure.](image)

Figure 1.3. Schematic of general resistive sensor device structure.

### 1.1.1.3 Thermal conductivity sensors

As described in section 1.2.2, thermal conductivity sensors are based on the transfer of heat from a device to a gas. The amount of heat transferred, and thus the temperature of the device, is related to the thermal conductivity of the gas. In the thermal conductivity sensors presented in [28-33], a resistive heater of some sort was used to heat the gas with the temperature change being measured directly by a resistance temperature detector (RTD) or thermocouple. The resistive heaters used in previous thermal conductivity sensors range from air-bridge, usually silicon or polysilicon [31-33], to standard, usually Pt [28-30], microheaters. The sensors described in this work measure the temperature change caused by thermal conductivity changes of the gas mixture, through the gas composition, directly without the use of an additional RTD.

### 1.2 Detection mechanism of wide bandgap resistive hydrogen gas sensors

The aim of this report is to identify the detection mechanism(s) driving 3C-SiC resistive hydrogen gas sensors. Although this detection mechanism is not yet fully understood, several hypotheses are proposed in this report. The first proposed detection mechanism involves the adsorption of H$_2$ on the sensor surface that, in turn, causes a change in the device resistance. The second proposed detection mechanism is based on heat being absorbed from the device by the gas, causing a characteristic change in temperature of the device thus affecting the device resistance. Background information behind both of these detection mechanisms will be presented below.

#### 1.2.1 Surface adsorption detection mechanism

The adsorption detection mechanism is based on the first reports of contact potential changes with changing ambient environments in Ge in 1953 [42]. The dangling bonds of a semiconductor surface can act as adsorption sites for gases. Thus H$_2$ may adsorb on the semiconductor surface, most likely dissociating in the process. The presence of H atoms on the surface can influence the transport of electrons in the semiconductor, producing a measurable change in the a resistive 3C-SiC sensor’s resistance.
1.2.1.1 Adsorption fundamentals

The adsorption of gaseous species on the surface of a solid is driven by either physical (van der Waals forces) or chemical bonding forces, termed “physisorption” and “chemisorption” respectively. The difference between these types of adsorption lie in the nature of the interaction. Physisorption is usually driven by physical forces such as Coulombic attraction whereas chemisorption is the actual sharing of electrons, forming a weak covalent bond. This difference is quantified by the surface binding energy, with bond energies greater than 10 kcal/mol (or 0.43 eV/molecule) attributed to chemisorption and bond energies less than 10 kcal/mol to physisorption [43].

The quantity of gas that adsorbs on a solid surface is a function of temperature, total pressure, and composition of the adsorbing gas near the surface. A plot of the amount of adsorbed gas, given in a variety of units from fractional surface coverage to volume of gas adsorbed per weight of solid (cc/g), versus partial pressure of that gas at a fixed temperature is termed an adsorption isotherm. Different adsorption isotherms are utilized to describe different adsorption mechanisms. For example, the Langmuir adsorption isotherm is used for non-interacting gases and with solids whose adsorption sites are all equivalent while the Tempkin adsorption isotherm is used for interacting gases [43].

The adsorption of gases on solid surfaces is not only a function of temperature, total pressure and composition as described above, but is also a function of the surface structure of the solid [43]. The surface structure of a solid is defined by the crystal plane and surface reconstruction of that surface. With tungsten (W), for example, N\textsubscript{2} readily adsorbs to the W(100), W(310), W(411), W(210), and W(311) crystal planes whereas very little adsorption of N\textsubscript{2} is found on W(110), W(211), W(111), and W(321) [43]. The adsorption of gases on a solid surface can also either induce a surface reconstruction or change a surface’s existing reconstruction. For example, upon the adsorption of CO onto a (2x1)Pt(110) surface, the surface atoms move to form a (1x1) surface reconstruction, and remains in that surface reconstruction even after CO desorbs from the surface [43].

1.2.1.2 H\textsubscript{2} induced surface metallization on 3C-SiC

In the 3C-SiC material system, it has been shown both experimentally and theoretically that the adsorption of hydrogen on the surface of 3C-SiC (001) induces a 3x2 surface reconstruction in ultrahigh vacuum (UHV). The band structure of 3C-SiC changes at the surface due to this induced surface reconstruction, bending the bands such that the conduction band crosses the Fermi level, as shown in Figure 1.4. With the Fermi level in the conduction band (at least at the surface) electrons no longer have an energy gap to cross and are free to move without restriction. Thus, the surface of 3C-SiC under these conditions becomes metallic in nature [44-46]. Under these conditions, an increase in electron flow (decreased resistance), at least at the surface, should be observable. The surface adsorption mechanism is one hypothesis to explain the detection mechanism driving 3C-SiC resistive hydrogen gas sensors. The second hypothesis, a thermal detection mechanism, is described below.
1.2.2 Thermal detection mechanism

The thermal detection mechanism is based on recent evidence showing the temperature of the resistive gas sensor changing while subjected to different gases [15]. With the absence of any other thermal phenomena (i.e. the latent heat associated with a phase change), the only manner for the temperature of the gas sensor to change is by heat transfer (from the device to the gas). The heat transfer properties of different gases can vary dramatically, as shown in Table 1.1 [47]. Since a semiconductor’s resistivity is strongly temperature dependent, even small changes in temperature can be detected as a change in resistivity.

| Table 1.1. Thermal properties of several gases at various temperatures [47]. |
|-----------------|-----------------|-----------------|-----------------|
|                 | \( k \) (W/m·K) | \( C_p \) (J/mol·K) | \( k \) (W/m·K) | \( C_p \) (J/mol·K) |
| Gas             | 300 K           | 600 K           | 300 K           | 600 K           |
| N\(_2\)         | 0.0222          | 0.0441          | 28.47           | 29.73           |
| Ar              | 0.0152          | 0.0301          | 20.81           | 20.81           |
| He              | 0.135           | 0.247           | 20.81           | 20.81           |
| H\(_2\)         | 0.156           | 0.291           | 28.73           | 29.75           |
| CH\(_4\)        | 0.0277          | 0.0948          | 36.8            | 51.25           |
| CO\(_2\)        | 0.0129          | 0.0403          | 37.64           | 47.9            |
| O\(_2\)         | 0.0225          | 0.0412          | 26.2            | 33.08           |
1.2.2.1 Heat transfer basics

The transfer of heat from the device to the gas can be analyzed by first writing a differential energy balance on a differential volume unit of the device, shown in equation 1.1 [48]. A glossary of terms and the full derivation of heat transfer equations used can be found in Appendix A.

\[ \rho C_p \frac{\partial T}{\partial t} = \sigma |\nabla V|^2 + k \nabla^2 T \]  

(1.1)

This energy balance describes the transport of energy inside the device, not its interaction with the gas. Boundary conditions are needed to completely define the heat transfer problem and define the interaction between the device and the gas. The first boundary condition defines the initial state of the system by defining the temperature of the device at \( t = 0 \), shown in equation 1.2. The second boundary condition, equation 1.3, defines the heat flux at the heater/device interface (see section 2.2.7 for details of the gas sensor packaging), which is constant for each experiment not utilizing temperature control. The final boundary condition defines the heat flux at all surfaces aside from the heater/device interface, shown in equation 1.4. The amount of heat transferred to the gas is described by Newton’s law of cooling, equation 1.4, and contains a heat transfer coefficient \( (h) \) that describes the heat transfer characteristics of the gas [48].

\[ T = T_o \]  

(1.2) 

\[ q_{heater/device} = \frac{q_{heater}}{q_{heater/device}} = -k \nabla T \bigg|_{heater/device} \]  

(1.3) 

\[ q_{surface} = h(T_{gas} - T_{surface}) = q_{surface} = -k \nabla T \bigg|_{surface} \]  

(1.4)

Heat transfer, as defined by equations 1.1 through 1.4, will occur at all times a gas sensor experiment is in progress. During a gas sensor experiment, the concentration of the test gas (\( H_2 \) in this case) is changed in relation to a dilutant gas (usually N\(_2\), Ar or air) while keeping the total flow over the sensor constant. With each change in the composition of the gas, the heat transfer characteristics of that gas change. The thermal properties, namely specific heat \( (C_p) \) and thermal conductivity \( (k) \), are a function of the gas composition and will always be between those of the pure components. Thus, the thermal properties of the test gas mixture will always be different from those of the pure dilutant gas. In this manner, the thermal detection mechanism is based on changes in thermal properties in relation to the dilutant or the “reference” gas. These changes in thermal properties, combined into the heat transfer coefficient, are measured as a temperature change due to the transfer of heat from the device to the gas.

1.2.2.2 Thermal conductivity of gas mixtures

The thermal conductivity of a gas mixture can be expressed by the empirical relationship proposed by Wassiljewa, shown in equation 1.5, where \( k_{mix} \) is the thermal

\[ k_{mix} = \sum_{i} \omega_i k_i \]  

(1.5)
conductivity of the mixture, \( n \) is the number of gases in the mixture, \( y_i \) is the mole fraction of gas \( i \), \( k_i \) is the thermal conductivity of pure gas \( i \), and \( A_{ij} \) is a function of the pure gas properties [49].

\[
k_{\text{mix}} = \sum_{i=1}^{n} y_i k_i \left( \sum_{j=1}^{n} y_j A_{ij} \right)
\]

(1.5)

The functional form of \( A_{ij} \) can be expressed using Mason and Saxena’s proposed expression in equation 1.6, where \( M_i \) is the molar mass of pure gas \( i \) [49].

\[
A_{ij} = \frac{1.605 \left[ 1 + \left( k_i / k_j \right)^{\frac{1}{2}} \left( M_i / M_j \right)^{\frac{1}{4}} \right]^2}{\left[ 8 \left[ 1 + M_i / M_j \right] \right]^{\frac{1}{2}}}
\]

(1.6)

The thermal conductivity of a He-N\(_2\) mixture as a function of He concentration at room temperature is presented in Figure 1.5.

![Figure 1.5: Thermal conductivity of a He-N\(_2\) mixture as a function of He mole fraction at room temperature [29].](image)

1.2.2.3 Temperature dependence of semiconductor resistivity

The temperature dependence of the resistivity of a semiconductor is related to both the concentration of electrons and holes \((n \text{ and } p = \text{[cm}^{-3}\text{]})) as well as their respective mobilities \((\mu_n \text{ and } \mu_p = \text{[cm}^2\text{/V} \cdot \text{s}])\), as shown in equation 1.7 [50].

\[
\rho = \frac{1}{\sigma} = \frac{1}{q(\mu_n n + \mu_p p)}
\]

(1.7)
Assuming the semiconductor is n-type, i.e. doped with donor atoms such that \( n \gg p \), the expression for resistivity simplifies to the expression found in equation 1.8. The same arguments presented below also stands for p-type semiconductors.

\[
\rho = \frac{1}{q \mu_n n}
\]  

(1.8)

Both the concentration of electrons and electron mobility are temperature dependent. A glossary of terms and the full derivation of the temperature dependence of carrier concentrations (electrons and holes) can be found in Appendix B.

The temperature dependence of the concentration of electrons stems from the thermal energy of the system, \( k_B T \). The concentration of electrons is given by equation 1.9, which contains two temperature dependent terms [51].

\[
n = 2\left(\frac{2\pi m_e k_B T}{\hbar^2}\right)^{3/2} e^{(E_f - E_c)/k_B T} \\
= N_c e^{(E_f - E_c)/k_B T}
\]  

(1.9)

The first term is the effective density of states for electrons which describes the number of electrons per unit volume that exist in the semiconductor. The second temperature dependent term describes the fraction of those electrons that will have enough energy to jump from the valence band to the conduction band. The combination of these two temperature dependent terms given in equation 1.9 yields three different regions, termed the freeze out, extrinsic, and intrinsic regions, of carrier concentration dependence on temperature, shown in Figure 1.6 for n-type Si.

![Figure 1.6. Temperature dependence of majority carrier concentration for n-type Si [51].](image-url)
In the first region, for \( T < \sim 100 \text{ K} \), very few donor atoms are ionized, and any electrons that can move have insufficient thermal energy to excite them from the valence band to the conduction band. This region of insufficient thermal energy is termed the freeze out region. The second region is termed the extrinsic region and applies to temperatures between 100 K and 450 K. The thermal energy within this temperature range causes essentially approximately all donors to be ionized, in Si, but not to possess enough energy to cross the bandgap. This gives a relatively constant carrier concentration over this span of temperatures. If the temperature is increased even further, \( T > \sim 450 \text{ K} \), electrons will have enough thermal energy to cross the bandgap with the carrier concentration approaching the intrinsic carrier concentration, thus termed the intrinsic region [51].

The other term that factors in the temperature dependence of resistivity of an n-type semiconductor is the electron mobility. The electron mobility is a measure of the ease of electron motion in a semiconductor. Several different scattering effects govern the magnitude of this mobility such as phonon and ionized impurity scattering. Phonon scattering refers to the collision between electrons and lattice vibrations while ionized impurity scattering refers to the Coulombic attraction or repulsion between electrons and the ionized donors. Other scattering mechanisms exist, but phonon and ionized impurity scattering are the dominant scattering mechanisms [51].

The first order approximation of the mobility caused by phonon scatter yields the inverse relationship shown in equation 1.10. As temperature increases, the lattice vibrations (or phonons) also increase, increasing the scattering of electrons and decreasing the electron mobility, as demonstrated in equation 1.10. However, increasing temperature increases the velocity at which electrons move. This increased velocity decreases the time in which their movement is influenced by ionized impurities. Thus, the mobility associated with ionized impurity scattering is directly proportional to temperature, as shown in equation 1.11. However, increasing temperature increases the number of ionized impurities, yielding the inversely proportional term in equation 1.11 [51].

\[
\frac{1}{\mu_n} = \frac{1}{\mu_{\text{phonon},n}} + \frac{1}{\mu_{\text{ionized},n}}
\]

(1.12)

Once the mobilities caused by the different scattering mechanisms have been determined, they are combined to form an overall mobility, shown in equation 1.12 [51].
ionized impurity scattering, but then increases with temperature due to the phonon
scattering as previously described [51-53].

Upon examination of the resistivity versus temperature plots in Figure 1.7, a doping
level for a resistive sensor based on the thermal detection mechanism can be selected.
For example, lower dopings, such as the unintentionally doped line for 3C-SiC in Figure
1.7a, have a higher temperature coefficient of resistivity at temperatures greater than 0°C,
however, this coefficient is not constant along all temperatures greater than 0°C.
Therefore, even with the highest change in resistivity for a given change in temperature,
that change will not be constant for all temperatures. This gives rise to a non-linear
sensor response. However, the degenerately doped line for 3C-SiC in Figure 1.7a has a
relatively constant temperature coefficient of resistivity but does not posses as high a
magnitude as the unintentionally doped line. Thus, there is a trade off between
sensitivity, magnitude of a change in resistivity due to a change in temperature, and
linearity.
Chapter 2: Resistive gas sensor fabrication

2.1 First generation devices

The fabrication process of first generation devices (devices fabricated prior to April 2004) is reported in detail in [54]. The general device structure, consisting of a 4 µm thick 3C-SiC epitaxial layer grown on n-type Si (001) with two planar contacts on the surface is shown in Figure 2.1. The 3C-SiC epitaxial layer was grown by low-pressure chemical vapor deposition (LPCVD), described in section 2.1.1. After the 3C-SiC epitaxial layer was grown, the samples were cleaned using a standard RCA process described elsewhere [55]. The contacts on these devices were fabricated using one of two schemes. The first scheme uses Kapton® tape to mask the “active area” of the sensor while the contacts were being deposited, described in section 2.1.2. The second scheme uses one photolithography mask, described in section 2.1.3. Both of these schemes are described in more detail below.

![Figure 2.1. Schematic drawing of 3C-SiC/Si gas sensor. The 3C-SiC film is 4 µm thick.](image)

2.1.1 3C-SiC/Si epitaxial growth

The 3C-SiC epi layer was grown on Si(001) in a horizontal LPCVD reactor [56]. The process involves three main steps. First, a native oxide H\textsubscript{2} etch of the silicon wafer was performed. This was followed by a carbonization step, which converts the Si surface to SiC. The final step is the growth of the 3C-SiC epi layer on the carbonized surface. Prior to growth, the Si wafer was RCA cleaned and placed on a graphite susceptor, which was inserted into the reaction tube. Purified hydrogen, with a flow of 9 SLM, was introduced at a pressure of 150 Torr. The susceptor and Si wafer were then heated by radio frequency (RF) induction to 1000°C and hydrogen etched in this manner for 10 min. The RF generator was then switched off for 5 minutes. Propane was then added to the hydrogen stream at a partial pressure of 0.03 Torr. After 60 sec, the RF generator was switched back on until the growth temperature of 1380°C was reached. After 90 sec SiH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8} were introduced at partial pressures of 0.035 and 0.035 Torr respectively. 3C-SiC growth was then conducted for 120 min after which the RF generator was turned off and the sample was cooled under an Ar flow to ambient temperature. A growth rate of ~
2µm/hour is typical for this process thus resulting in a 4 µm film for subsequent gas sensor fabrication [14,40].

2.1.2 Scheme 1 – Kapton® tape mask

Kapton® is a polyimide film, developed by DuPont®, that is able to withstand temperatures up to 400°C [57]. Kapton® tape was folded over on itself so there was no exposed adhesive, cut to the desired thickness, and then placed on the sample surface. Both sides of the folded over Kapton® tape were then taped to a support wafer to hold the sample and Kapton® tape “mask” in place. The samples were then placed in the electron-beam evaporator for the deposition of ~ 2000 Å of NiCr. After the deposition, the Kapton® tape was removed, the sample was rinsed in acetone and DI water then dried in nitrogen (N₂). The sample was then annealed in a rapid thermal processing (RTP) unit at 950°C for 2 minutes, in order to form ohmic NiCr contacts with linear current versus voltage (I-V) characteristics shown in Figure 2.2. These devices where then loaded onto a ceramic sample holder, contacted to with Ni probes, and placed in the first generation gas sensor test bed described in section 3.1.

![Figure 2.2. Current versus voltage (I-V) characteristics of a typical first generation 3C-SiC resistive hydrogen gas sensor.](image)

2.1.3 Scheme 2 – Photolithography mask

In this scheme, the photolithography mask shown in Figure 2.3 was used in conjunction with negative photoresist (NR1-PY 3000 from Futurrex Inc.) to form the NiCr contacts. This negative photoresist was spun on the sample surface at 3000 RPM for 40 seconds followed by a soft bake for 60 seconds at 155°C. After the device cooled, the mask shown in Figure 2.3 was aligned to the sample and exposed using UV radiation, using a Quintel mask aligner, for 17 seconds followed by a post-exposure bake for 60 seconds at 130°C. After the device cooled, the photoresist was developed in RD6 for 20 seconds, from Futurrex Inc., after which the device was rinsed in de-ionized (DI) water then dried in nitrogen (N₂). The samples were taped to a Si wafer (for support) and placed in the electron-beam evaporator for the deposition of ~ 2000 Å of NiCr. After the deposition, the unwanted NiCr was removed using a standard lift-off process by rinsing...
in acetone to dissolve the remaining photoresist. After all the unwanted metal was removed, the samples were rinsed in methanol and DI water then dried in N\textsubscript{2}.

![Figure 2.3. Photolithography mask used for first generation devices.](image)

After the contacts were deposited on the sample surface, the contacts were annealed in a RTP at 950°C for 2 minutes to produce ohmic NiCr contacts. After the NiCr contacts were made ohmic, negative photoresist was again spun on the sample surface. The same mask shown in Figure 2.3 was aligned to the existing NiCr contacts, and exposed then developed using the process described above. The samples were again taped to a Si support wafer and placed in an electron-beam evaporator for the deposition of a Ti (100 Å) / Au (1800 Å) stack. The Ti/Au stack is required for Au wire bonding to the device [55]. The unwanted metal was removed using the lift-off process described above. The samples where then mounted in a ceramic package with Au leads that were wire bonded to the contacts on the device. These leads were contacted to with Ni wire and stainless steel screws to allow for electrical connections, and placed in the first generation gas sensor tested bed described in section 3.1.

2.2 Second generation devices

For the second generation devices, a four-layer photomask set was designed and fabricated. The evolution to a full photolithography fabrication process allows for the control of device dimensions to within a few micrometers. This four-layer mask set contains resistive, Schottky diode and/or capacitor, van der Pauw, and transmission line method (TLM) structures. The TLM and van der Pauw structures can be used for contact and material characterization whereas the resistive, Schottky diode and capacitor structures allow for gas sensing device fabrication.

The TLM structures have a constant contact size (50 x 100 µm), but with increasing distances between them (10 to 50 µm in 5 µm steps). The van der Pauw structures have four square contacts, measuring 1 mm on a side, but with several gap sizes (0.25, 0.5, and 1 mm). Resistive devices on the mask were made from the 64 combination of 3 parameters, contact width (x), contact height (y), and gap length (L), with 4 different dimensions, 0.25, 0.5, 1, and 2 mm. These resistive devices were then grouped in several ways, i.e. devices with a constant exposed area were grouped as well as devices with the same gap length and contact width, and placed on the mask. The Schottky diode and capacitor devices consist of dots with diameters of 250, 500, 750, and 1000 µm.

The various device dimensions for the mask set previously described were chosen to aid in the investigation of the mechanism driving 3C-SiC resistive gas sensors. Devices with the same contact dimensions but increasing gap lengths, i.e. 0.25 mm, 0.5 mm and 1
mm, are used to test the surface adsorption detection mechanism presented in section 1.2.1. With constant contact dimensions, any gas detection caused by the contacts should be constant for all devices. Thus, any differences in response can be attributed to the increasing exposed surface areas through the surface adsorption detection mechanism. However, increasing the gap length increases the device resistance \( R = \rho L / A \), which decreases the amount of Joule heating for a fixed voltage \( P = V^2 / R \). This will factor into the thermal detection mechanism presented in section 1.2.2. In this way, devices with constant exposed surface areas but different contact areas can be used to assess the influence of contact dimensions on device performance.

The four mask layers consist of 1) Active area definition, 2) Metal layer 1, 3) Metal layer 2, and 4) Contact pad metal. Mask layer 1, the active area definition, is performed for all devices, whereas the application of the other three mask layers is dependent on the experiment. An example device layout for the four-layer mask previously described, utilizing the Active area definition, Metal layer 1, and Contact pad metal layers, is shown in Figure 2.4. The full fabrication scheme is described below.

![Active area definition, Metal layer 1, Contact pad metal](image)

**Figure 2.4. Example second generation device layout.**

### 2.2.1 Resistive sensor fabrication process

A schematic of the device structure used for second generation devices is presented in Figure 2.5. The fabrication process for these second generation devices starts with the epitaxial growth of a 1.4 \( \mu m \) thick 3C-SiC layer on a thin Si layer bonded to a polycrystalline SiC wafer by a process described in section 2.2.2. After epitaxial growth, these samples were RCA cleaned, which rids the sample surface of most organic and metallic atoms/molecules [55]. Next, the surface is covered with \( \approx 5000 \) Å of silicon dioxide \((SiO_2)\) via plasma enhanced chemical vapor deposition (PECVD). The rest of the fabrication process is described below.

### 2.2.2 3C-SiC/SOI epitaxial growth

A thin 3C-SiC film was deposited on a thin Si (001) layer (~ 150 Å) miscut 4° towards the [211] direction, bonded to a polycrystalline SiC substrate, which is referred to as silicon-on-insulator (SOI), using a wafer bonding process described elsewhere [56]. The SOI substrate was RCA cleaned prior to deposition to remove trace organic and
metal species from the surface [55]. The 3C-SiC deposition was carried out in a low-pressure, hot-wall, horizontal chemical vapor deposition (CVD) reactor using the traditional dual precursor gas chemistry, propane (C\textsubscript{3}H\textsubscript{8}) and silane (SiH\textsubscript{4}) [58]. Hydrogen chloride (HCl) was also incorporated into the gas stream as a growth promoter. During the CVD process, a gas stream containing C\textsubscript{3}H\textsubscript{8} and H\textsubscript{2} was established in the chamber while the sample temperature was ramped from room temperature to the growth temperature of 1360°C. Once at the growth temperature, the process pressure was lowered to 200 Torr after which SiH\textsubscript{4} and HCl were added to the gas stream for growth. The Si/C and Si/Cl ratios during growth were set to 0.7 and 3.3, respectively. The 3C-SiC epitaxial film was determined to be ~ 1.4 μm thick measured via FTIR [59].

2.2.3 Active area definition

The active area definition mask is used to etch “windows” in the SiO\textsubscript{2} layer to define the “active area” of the gas sensor. After the deposition of the SiO\textsubscript{2} layer, the sample is placed in a 3:1 mixture of H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2}, “Piranha etch,” for 1 minute. The sample is then rinsed in DI water and dried in N\textsubscript{2}. A dehydration bake was then performed on the sample by placing it on a hot plate at a temperature ~ 150°C for 5 minutes to remove any remaining water from the surface. After the sample cools, it is then placed on a spinner. Hexamethyldisilazane (HMDS) is then placed on the sample surface and allowed to stand for ~ 1 minute, after which it is spun at 3000 RPM for 30 seconds. Next, Shipley 1813 positive photoresist is spun on the sample surface at 3000 RPM for 30 seconds followed by a softbake at 110°C for 60 seconds. Next, the active area mask is aligned to the sample and exposed for 21.5 seconds on the Quintel mask aligner. The photoresist is then developed in MF-319 for approximately 2 minutes, then rinsed in DI water and dried in N\textsubscript{2}. The photoresist is then hardbaked at 110°C for 60 seconds.

After the sample cools, it is placed in a 10:1 buffered oxide etch (BOE) for ~ 15 minutes to etch the windows in the 5000 Å thick SiO\textsubscript{2} layer to define the active area of the sensors. After the BOE etch is finished, the samples are rinsed in DI water, but not dried. They are then placed in a 3:1 Piranha solution (described above) for 60 seconds to remove the remaining photoresist. After the photoresist is removed, the samples are again rinsed in DI water and dried in N\textsubscript{2}. The samples are then ready for the next photolithography step.
2.2.4 Metal layer 1

After the sensor active areas have been defined, metal must be deposited, in controlled regions, to form the ohmic contacts for the sensor. If the samples were not processed immediately following the active area definition step, the samples were dipped in a 3:1 Piranha solution for 60 seconds, then rinsed in DI water and dried in N\textsubscript{2}. Next, another 5 minute dehydration bake was performed. After cooling, the sample is placed on the spinner and Futurrex Inc. negative photoresist NR9-1500PY is spun on the surface at 3000 RPM for 40 seconds, followed by a softbake at 155°C for 60 seconds. The metal layer 1 mask is then aligned to the alignment marks etched in the SiO\textsubscript{2} layer formed with active area definition mask (described in section 2.2.3) and exposed for 7.5 seconds, followed by a post-exposure bake at 110°C for 60 seconds. The photoresist is then developed in RD6 for 20 seconds, rinsed in DI water and blown dry with N\textsubscript{2}.

After the photoresist is developed on the sample surface, the metal layer 1 is ready to be formed by depositing metal on the sample. This deposition was performed either by electron-beam evaporation or by sputtering. For all resistive samples, ~ 2000 Å of NiCr was deposited, usually by electron-beam evaporation. After the metal layer is deposited, the unwanted metal is removed by a lift-off process. This lift-off process included either the submersion of the sample in resist remover, RD4 from Futurrex Inc. at ~ 110°C, or by sonicating the sample in acetone for several minutes. After all of the unwanted metal is removed from the sample surface, the sample is rinsed several times in acetone and methanol, then in DI water and dried in N\textsubscript{2}. For resistive sensors, the contacts are then annealed in a RTP at 950°C for 2 minutes.

2.2.5 Metal layer 2

The fabrication process for metal layer 2 is the same as for metal layer 1 in all respects. This metal layer allows the deposition of two different metals on the same sample, thus giving the possibility of testing both of their responses to the detection gas. For example, a resistive sensor with NiCr contacts could be tested alongside Schottky diode sensors with a Pd gate on the same sample. This would allow the detection of low concentrations of H\textsubscript{2} using the Schottky diode sensor [19,38] as well as high concentrations of H\textsubscript{2} using the resistive sensor [14].

2.2.6 Contact pad metal

The contact pad metal layer was fabricated using one of two different masks depending on the application. The contact pads consist of a Ti (200 Å) / Au (4000 Å) stack. The Ti aids in adhesion, and Au allows for wire bonding. Using the contact pad metal mask, the Ti/Au stack is deposited on the metal 1 layer that overlaps the SiO\textsubscript{2} layer, as seen in Figure 2.4. The second scheme uses the metal layer 1 mask to completely cover the contacts with the Ti/Au bonding layer. For this contact pad metal layer, the same negative photoresist process outlined in section 2.2.4 is used but with the Ti/Au stack being the metal deposited and with no annealing afterwards.

2.2.7 Packaging

After fabrication, sensor samples were diced into pieces measuring ~ 3 mm x 6 mm and mounted in a 16-pin gold package. Each sample was mounted to a resistance temperature detector (RTD) which is mounted to a ceramic heater. The contacts of the
sensors, fabricated using the second generation fabrication process described above, are wire bonded to the package pins using a ball bonder. This new packaging scheme was employed to measure the temperature of the device, via the RTD, and control its temperature with the ceramic heater. The packaging of these devices was performed by Evald Mildh at Linköping University in Sweden.

2.3 Problems with second generation fabrication process

The only problem with this second generation fabrication process lies in the potential for the metal on the semiconductor surface not being in contact with the metal on the SiO$_2$ surface. The metal in metal layers 1 and 2 overlap the active area definition by 200 μm on three sides of the contacts. This was done so the contact pad metal could be deposited on metal layers 1 and 2 without depositing on the metal that is in contact with the semiconductor surface (the active area). The problem lies in the fact that the SiO$_2$ layer is ~5000 Å thick, and the metal layers are usually ≤2000 Å thick. Then the metal layer is deposited, there is no guarantee that the metal on the substrate will contact the metal on the SiO$_2$, as shown in Figure 2.6.

![Figure 2.6. Schematic of fabrication problems using second generation process.](image)

To alleviate this problem, the second scheme outlined in section 2.2.6 was developed and utilized by using the metal 1 layer mask to deposit the bonding layer over the entire contact area to generate the contact pads. The metal 1 and metal 2 could also be deposited via sputtered instead of electron-beam evaporation. Sputtering the metal layer would coat the side-walls of the field oxide layer, giving good contact between the metal on the field oxide and the metal on the semiconductor surface.
Chapter 3: Gas sensor test beds

3.1 First generation test bed

The first generation test bed is described in detail in [54]. This test bed consists of a tube furnace, three mass flow controllers (MFCs), three solenoid valves, a power supply, and a digital multimeter (DMM), shown in Figure 3.1. The sensors are placed in a 1” diameter quartz tube which resides in a tube furnace. The furnace controls the temperature of both the gas and of the sensor. The mass flow controllers are controlled by an analog output card, through a MFC readout, and the solenoid valves are controlled by a digital input/output card, through an electromechanical relay module. Both the analog output and digital input/output cards are installed in a computer. The power supply and digital multimeter are also controlled by a computer via GPIB and serial communication respectively. The power supply biases the gas sensor while the DMM measures the voltage across the sensor, the current flowing through the sensor, and the temperature of the gas around the sensor. Due to the nature of the measurements, different measurement modes and channels in the DMM, data was collected at a sampling frequency of 0.5 Hz. All of these components are controlled by a computer through Labview from National Instruments.

![Figure 3.1. First generation gas sensor test bed.](image)

3.2 Second generation test bed

The second generation test bed was developed to accommodate the sensor packaging described in section 2.2.7. The pins of the 16-pin gold package can only be contacted to using a printed circuit board (PCB) which cannot be heated above 125°C [60]. With the maximum operating temperature of the PCB being 125°C, the PCB cannot be placed in the quartz tube used in the first generation test bed described above. Thus, an aluminum housing was fabricated to support the sensor package and allow gas to flow over the sensor. This aluminum housing provides only an ~ 7 mm (0.157”) space for gas to flow over the sensor, greatly decreased from the first generation test bed described in section 3.1. This test bed was expanded to accommodate 6 MFCs, all of which are computer controlled, shown in Figure 3.2. In place of the digital multimeter, an 18-bit 16 channel...
an analog input card was added to the computer, which also drastically increased the sampling rate from 0.5 Hz to 10 Hz with 500 kHz sampling rates possible.

Figure 3.2. Second generation gas sensor test bed.

3.2.1 Electronic circuits

3.2.1.1 Gas sensor and ceramic heater circuits

A simple operational amplifier follower circuit, shown in Figure 3.3 is used to supply the bias to the gas sensor in place of the power supply. The OPA541 operational amplifier (op amp), available from Texas Instruments (TI), is capable of up to 10 A of output current. The current flowing through the sensor (RV) is determined by the voltage drop across a precision resistor (RC). The precision resistor was either 1±0.02% Ω or 100±0.005% Ω. The resistor RB ensures the voltage at the non-inverting input of the op amp to be grounded if $V_{\text{in}}$ is disconnected. The ceramic heater is powered by the same circuit that drives the gas sensor, shown in Figure 3.3, with the heater as RV and a 0.01 Ω resistor as RC.

Figure 3.3. Second generation test bed circuit.
3.2.1.2 RTD circuit

The RTD measurements were performed by the combination of a XTR105, 4-20 mA current transmitter with sensor excitation, and RCV420, precision current loop receiver, integrated circuits (ICs) from TI. The XTR105 passes a known current (nominally 800μA) through the RTD and a matched current through a reference resistor. The voltage drop across the reference resistor is subtracted from the voltage drop across the RTD, then multiplied by a gain and linearized to produce a 4-20 mA signal that is proportional to an initial temperature, set by the reference resistor, and a temperature span, set by the gain. This 4-20 mA signal is then passed to the RCV420 which converts it to a 0-5V signal that is measured by the PCI-6281 analog card previously described.
Chapter 4:  Results

4.1  First generation 3C-SiC sensors

Initial hydrogen gas sensing experiments performed on 3C-SiC/Si sensors demonstrated the potential of 3C-SiC as a hydrogen gas sensing material. The fabrication of these devices is described in section 2.1 while the gas sensor test bed is described in section 3.1. For example, Figure 4.1 shows the response, reported as the change in current relative to 0% H\(_2\), of two 3C-SiC/Si sensors with constant contact areas but different gap lengths, 0.5mm and 1 mm, to high concentrations (10% to 100%) of H\(_2\) in Ar at 50°C. Initial experiments aimed at determining the detection mechanism suggested the surface adsorption mechanism discussed in section 1.2.1. The sensor responses shown in Figure 4.1 approximately scaled with exposed SiC area (ratio between areas = 2:1 whereas the ratio between sensor responses ~ 1.5:1). The increased surface area can give an increased opportunity for H\(_2\) to influence the surface conductivity, a result depicted in Figure 4.1. These results are discussed in more detail in Chapters 5 and 6.

![Figure 4.1. Gas sensor response at 50°C to H\(_2\) in varying concentrations (10%-100% with 10% increments) with Ar purge between H\(_2\) events. Dashed line L = 0.5 mm, solid line L = 1 mm.](image)

4.2  Second generation 3C-SiC sensors

Several experimental improvements were made for the second generation sensors in an effort to determine the gas sensing mechanism. First, a thin film (1.4μm) of 3C-SiC deposited on an insulating substrate, described in section 2.2.2, was used in these studies. The use of a thin film on an insulating substrate allows for better control of where current flows in the device, i.e. only through the 3C-SiC epi-layer and not also through the Si substrate. Also, fabricated devices had an improved structure with the addition of a field oxide isolation layer with a four-layer photolithography mask set, discussed in section
2.2. The packaging of second generation sensors, discussed in section 2.2.7, also allowed for device temperature measurement and control.

Figure 4.2 shows the current flowing through a 3C-SiC/SOI sensor and Figure 4.3 shows the device temperature while exposed to high concentrations (10% to 100%) of H$_2$ in N$_2$ at 400°C. Figure 4.3 shows drastic decreases in device temperature upon the introduction of H$_2$ to the system. These decreases in device temperature cause changes in the resistivity of the 3C-SiC epi-layer which in turn cause a change in the current passing through the device at a fixed voltage, as seen in Figure 4.2. With these changes in device temperature, the thermal detection mechanism outlined in section 1.2.2 seems to drive the gas sensing of these 3C-SiC sensors.

![Figure 4.2. Current (left axis) and percent change in current (right axis) flowing through a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to various concentrations (10% to 100% in 10% increments) of H$_2$ in N$_2$ at an initial device temperature of 400°C and a bias of 10 V DC.](image1)

![Figure 4.3. Temperature of a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to various concentrations (10% to 100% in 10% increments) of H$_2$ in N$_2$ at an initial device temperature of 400°C and a bias of 10 V DC.](image2)

When device temperature is controlled, the current flowing through a 3C-SiC/SOI sensor increases with the introduction of H$_2$ to the system, as shown in Figure 4.4. This increase in current is opposite of that when device temperature is not controlled as shown in Figure 4.2. This opposite behavior initially suggests another detection mechanism. However, the current also increases when increasing concentrations of He are introduced in a Ar atmosphere as shown in Figure 4.5. Since He and Ar are monatomic noble gases, they should have similar interactions with the surface, allowing any surface adsorption effects to be ignored. Since changes in current are still observed in Figure 4.5, and the thermal properties, mainly thermal conductivities are so different, the thermal detection mechanism still explains the detection. These results are discussed in more detail in Chapters 7 and 8.
Figure 4.4. Current flowing through a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to 10% to 100% H\textsubscript{2} (in N\textsubscript{2}) in 10% increments with device temperature controlled at 400°C and a bias of 10 V DC. Dotted line = H\textsubscript{2} on, dotted line with circle = H\textsubscript{2} off.

Figure 4.5. Current flowing through a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to 10% to 100% He (in Ar) in 10% increments with device temperature controlled at 100°C and a bias of 10 V DC.
Chapter 5: Hydrogen gas sensors using 3C-SiC/Si epitaxial layers

T. J. Fawcett¹, J. T. Wolan*¹, R. L. Myers², J. Walker² and S. E. Saddow²

¹ Chemical Engineering Department, University of South Florida, Tampa, FL 33620, USA
² Electrical Engineering Department, University of South Florida, Tampa, FL 33620, USA

Abstract. A hydrogen gas sensor consisting of planar electrical NiCr contacts formed on the surface of a 3C-SiC epitaxial layer grown on Si(001) has been fabricated and tested. The n-type, 4 µm thick 3C-SiC epi layer was grown under low-pressure conditions with an approximate doping density of $10^{18}$ cm$^{-3}$. This sensor demonstrates a two-fold repeatable improvement in stability and sensitivity in comparison to an n-type Si sensor of the same type also fabricated and tested under the same conditions. Both the 3C-SiC/Si and Si sensors operated up to 250 ºC; however, the 3C-SiC/Si sensor was able to detect hydrogen at concentrations far exceeding that of the Si sensor. The 3C-SiC/Si device detected hydrogen at concentrations ranging from 0.333% to 100% in Ar while the Si sensor could only detect hydrogen at concentrations ranging from 2% to 100% in Ar. Based on this preliminary data, it has been shown that 3C-SiC/Si hydrogen sensors of this type have a larger dynamic range and higher sensitivity to hydrogen than Si sensors, thus allowing for harsh environmental applications.

5.1 Introduction

High temperature extreme environment solid-state gas sensing is of great interest to the automotive, aerospace and chemical processing industries [6,17]. The wide bandgap, high thermal conductivity and thermal and chemical stability make silicon carbide (SiC) an ideal solid-state gas sensing material for operation under “harsh” conditions [22,61]. According to literature, a silicon (Si) gas sensor reportedly failed between 200ºC and 250ºC because of its relatively small bandgap of 1.1 eV [8,19,61]. This gives a 3C-SiC gas sensor (bandgap = 2.36 eV), the potential to operate at far greater temperatures. The 3C-SiC polytype was chosen because of its high electron mobility (~$10^3$ cm$^2$/V-sec) and ability to be epitaxially grown on Si, thus greatly decreasing the cost of wafers in comparison to bulk 3C-, 4H- or 6H-SiC substrates [20].

5.2 Epitaxial growth of 3C-SiC on Si(001)

In this work, a 3C-SiC epi layer was grown on Si(001) in a low-pressure horizontal cold-wall CVD reactor [56]. The process involves three main steps. First, a native oxide
H₂ etch of the silicon wafer was performed. This was followed by a carbonization step, which converts the Si surface to SiC. The final step is the growth of the 3C-SiC epi layer on the carbonized surface. Prior to growth, the Si wafer was RCA cleaned and placed on a graphite susceptor, which was inserted into the reaction tube. Purified hydrogen, with a flow of 9 SLM, was introduced at a pressure of 150 Torr. The susceptor and Si wafer were then heated by radio frequency (RF) induction to 1000°C and hydrogen etched in this manner for 10 min. The RF generator was then switched off for 5 minutes. Propane was then added to the hydrogen stream at a partial pressure of 0.03 Torr. After 60 sec, the RF generator was switched back on until the growth temperature of 1380°C was reached. After 90 sec SiH₄ and C₃H₈ were introduced at partial pressures of 0.035 and 0.035 Torr respectively. 3C-SiC growth was then conducted for 120 min after which the RF generator was turned off and the sample was cooled under an Ar flow to ambient temperature. A growth rate of ~ 2µm/hour is typical for this process thus resulting in a 4 µm film for subsequent gas sensor fabrication.

5.3 3C-SiC/Si gas sensor fabrication and testing

The gas sensing device was fabricated by evaporating NiCr (2000 Å) equipotential contacts on the 3C-SiC face of the structure. The device was then annealed at 950°C for 2 minutes in an Ar atmosphere to produce ohmic contacts. 5 shows a schematic drawing of the 3C-SiC/Si gas sensor. An n-type Si(001) sensor was also fabricated in the same manner and simultaneously tested for comparison. Both sensors were approximately 1 cm x 1 cm, with 2.5 mm wide contacts with an 5 mm wide gap between the contacts. The initial resistances of the 3C-SiC/Si and Si devices were approximately 13 Ω and 16.6 Ω respectively. The two sensors were placed in a gas sensor test bed, shown in Figure 5.2. Both sensors were biased with 2V using a Hewlett-Packard model 6626A quad programmable power supply. The sensors were exposed to UHP H₂ to determine sensor response at varying concentrations (0.333% to 100%) of H₂ in Ar with pure Ar flows in between each H₂ concentration to allow for complete desorption. The temperature of the test bed was varied from 50°C to 250°C in 50°C increments. The current flowing through each sensor was measured by a Keithley model 2700 Digital Multimeter (DMM) equipped with a Keithley model 7700 20-Ch. Multiplexer.

Figure 5.1. Schematic drawing of 3C-SiC/Si gas sensor. The 3C-SiC film is 4 µm thick.

Figure 5.2. Gas sensor test bed.
5.4 Results and discussion

The 3C-SiC/Si sensor was observed to be a great deal more sensitive to H\textsubscript{2} concentration than the Si sensor throughout the temperature range tested in this work. The gas sensor response in figures 2.3-2.6 (ΔI) is the change in current of each device relative to the current in 100% Ar (0% H\textsubscript{2}). Figure 5.3 illustrates the sensor response to various H\textsubscript{2} concentrations (10% to 100% in 10% increments) at 50°C with an Ar purge between H\textsubscript{2} events to allow for desorption. It can be clearly seen that at 10% H\textsubscript{2}, the 3C-SiC/Si sensor gave an approximately two-fold greater response than the Si sensor; while at 100% H\textsubscript{2}, the 3C-SiC/Si sensor showed approximately 3.5 times the response of the Si sensor. The Si sensor also saturated at about 40% H\textsubscript{2} in Ar, thus not allowing for reliable detection beyond this concentration. Figure 5.4 and Figure 5.5 show the 3C-SiC/Si and n-type Si(001) gas sensor response respectively to various concentrations of H\textsubscript{2} at various temperatures. Both sensors show a decrease in response, indicating a loss of sensitivity, as temperature increases. An empirical least squares fit to the relation between 3C-SiC/Si gas sensor response and H\textsubscript{2} concentration shown in Figure 5.4 is shown in Table 5.1.

The 3C-SiC/Si sensor showed the ability to detect extremely low concentrations of H\textsubscript{2} in Ar, while the Si sensor was limited in its concentration limits. The sensor response at low concentrations (0.333%, 0.5%, 1%, 2%, 3%, 4%, 4.7%, 5%, 7.5% and 10% H\textsubscript{2} in Ar) is shown in Figure 5.6. The total gas flow for these low concentrations was not kept constant (due to mass flow controller limitations). Thus there is no correlation between gas sensor response amplitude and H\textsubscript{2} concentration. This leads to the conclusion that the adsorption process is mass transfer limited. The 3C-SiC/Si sensor was able to detect H\textsubscript{2} down to 0.333% H\textsubscript{2} in Ar, while the Si sensor was only able to detect down to 2% H\textsubscript{2} in Ar.

![Figure 5.3. Gas sensor response at 50ºC to various concentrations of H\textsubscript{2} (10% to 100% with 10% steps). Solid line denotes 3C-SiC/Si response, dashed line Si response.](image1)

![Figure 5.4. 3C-SiC/Si gas sensor response vs. H\textsubscript{2} concentration at various temperatures.](image2)
Figure 5.5. n-type Si(001) gas sensor response vs. H$_2$ concentration at various temperatures.

Figure 5.6. Gas sensor response at low H$_2$ concentrations at 50ºC.

Table 5.1. Empirical relationships between 3C-SiC/Si sensor response to H$_2$ concentration at various temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Empirical fit</th>
<th>$R^2$ Correlation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>50ºC</td>
<td>$\Delta I = -0.0089[C_{H_2}]^2 + 0.017[C_{H_2}]$</td>
<td>0.9842</td>
</tr>
<tr>
<td>100ºC</td>
<td>$\Delta I = -0.0028[C_{H_2}]^2 + 0.0068[C_{H_2}]$</td>
<td>0.9937</td>
</tr>
<tr>
<td>150ºC</td>
<td>$\Delta I = -0.0008[C_{H_2}]^2 + 0.0027[C_{H_2}]$</td>
<td>0.9990</td>
</tr>
</tbody>
</table>

Note: $\Delta I$ [mA] and $C_{H_2}$ [% H$_2$ in Ar]

5.5 Conclusions

The 3C-SiC/Si gas sensor showed to be more sensitive to H$_2$ concentration than the n-type Si(001) sensor. The empirical relationships shown in Table 5.1 allow for the determination of H$_2$ concentration by measuring the current relative to 0% H$_2$. The 3C-SiC/Si gas sensor also showed no H$_2$ saturation effects allowing for the practical application in real-time H$_2$ concentration measurements.

5.6 Acknowledgements

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Chapter 6: Wide-range (0.33 – 100%) 3C-SiC resistive hydrogen gas sensor development

Timothy J. Fawcett and John T. Wolan
Chemical Engineering Department, University of South Florida, Tampa, Florida 33620

Rachael L. Myers, Jeremy Walker, and Stephen E. Saddow
Electrical Engineering Department, University of South Florida, Tampa, Florida, 33620


Abstract. Silicon carbide (SiC) resistive hydrogen gas sensors have been fabricated and tested. NiCr planar ohmic contacts were deposited on both a 4 μm 3C-SiC epitaxial film grown on n-type Si(001) and directly on Si to form the resistive sensor structures. Detection at concentrations as low as 0.33% and as high as 100% (H₂ in Ar) was observed with the 3C-SiC sensor while the Si sensor saturated at 40%. The 3C-SiC sensors show a remarkable range of sensitivity without any saturation effects typically seen in other solid-state hydrogen gas sensors. Under a constant 2 V bias, these sensors demonstrated an increase in current up to 17 mA upon exposure to pure H₂. Preliminary experiments aimed at determining the gas sensing mechanism of these devices have been conducted and are also reported.

6.1 Introduction

Hydrogen gas sensing is of great interest to the fuel cell, automotive, and aerospace industries, mainly for leak detection [1,18]. The aerospace and automotive industries require hydrogen sensors that can operate at high temperatures and under potentially corrosive conditions [6,18]. Silicon based sensors only operate up to 250ºC because of the relatively small bandgap of Si (1.1 eV) [7]. For operation at temperatures greater than 300ºC and in “harsh” environments, silicon carbide (SiC) sensors have been employed [38]. The wide bandgap (~2.2 eV for the 3C polytype), high thermal conductivity, and high chemical stability make SiC a gas sensing material of choice for extreme environments [18].

Resistive, or surface conductivity, gas sensors have mainly found their place in semiconducting oxide-based gas sensors [12]. The resistance of these semiconducting oxide materials is dependent on the adsorption of gases on its surface. The surface resistance is lowered by the adsorption of reducing gases and increased upon the adsorption of oxidizing gases in n-type semiconductor oxide sensors, allowing for the presence of reducing or oxidizing gases to be easily detected [36,62]. In this report, the
fabrication and testing of non-oxide-based resistive gas sensors fabricated from SiC will be reported.

6.2 Device fabrication

3C-SiC resistive gas sensors were fabricated by growing a 4 μm thick 3C-SiC thin film on n-type Si(001) by low pressure chemical vapor deposition (LPCVD). NiCr planar contacts were deposited by electron beam evaporation and then annealed for two minutes at 950°C in an Ar atmosphere producing a device showing good linear current versus voltage characteristics with a resistance of approximately 13 Ω. Identical Si sensors with NiCr contacts were fabricated from the same n-type Si(001) substrate that the 3C-SiC films were grown on to serve as a control, also giving linear current versus voltage characteristics with a resistance of approximately 15 Ω. A schematic of the 3C-SiC resistive sensor is shown in the insert of Figure 6.1. Both devices were mounted on ceramic sample holders with Ni probes contacting to the devices. These devices were then simultaneously placed in a quartz tube for testing under different gaseous atmospheres. A more detailed description of the epitaxial growth, device fabrication, and gas sensor testing apparatus can be found in Ref. [63].

6.3 Results and discussion

The change in resistance, of both the 3C-SiC and n-type Si(001) gas sensors, was monitored by recording the current flowing through each sensor while under a constant 2V DC bias. Figure 6.1 shows the sensor response at 50°C (relative current measured with respect to 0% H₂) to varying concentrations of H₂, from 10%-100% in 10% increments. It can be clearly seen that the 3C-SiC sensor shows a two-fold increase in response compared to that of the n-type Si(001) sensor. Both the 3C-SiC and Si sensors reach their respective maximum response within 15 minutes following a change in target-gas concentration. This response time is slow compared to other SiC based gas sensors (on the order of milliseconds [6]) because the response time of these resistive gas sensors is controlled by the adsorption kinetics, not the device structure. The only parameters that affect the adsorption kinetics are the concentration of the adsorbing species and the temperature of operation. However, the sensors reported here are capable of sensing hydrogen from below the combustion limit to 100%, whereas other SiC sensors are typically limited to concentrations below 10% [64].

Figure 6.2 shows the relative current versus time of the same sensors to various concentrations of H₂ also at 50°C. The concentration of H₂ was varied from 10% to 100% in Ar (in 10% increment) without an Ar purge between events to allow the desorption of hydrogen from the surface. Both the 3C-SiC and Si sensors show a reversible response with no need to the allow hydrogen to desorb from the semiconductor surface. This allows either of these sensors to be used in an environment where the concentration of H₂ is continuously changing without losing the sensitivity due to any previous environment. Figure 6.2 also shows the Si sensor becoming saturated with H₂ at a concentration ~40% in Ar, rendering the Si sensor useless for detecting H₂ at concentrations above 40%. The 3C-SiC sensor does not show any saturation effects, making it useful for the detection of any H₂ concentration above 0.33% [63].

The specific gas sensing mechanism for this SiC resistive sensor system is still under investigation. One possible mechanism could be a reduction in the surface resistance due
to the molecular adsorption of H\textsubscript{2} onto the semiconductor surface, similar to the mechanism for the detection of reducing gases for the semiconducting oxide based sensors [36,62]. Another possible mechanism could be the catalytic dissociation of H\textsubscript{2} on the surface of the metal contacts. The atomic H then diffuses through the metal to the metal-semiconductor interface creating a dipole layer at the interface, changing the electrical properties of the device. This mechanism has been put forth to explain the detection of H\textsubscript{2} in Schottky barrier diode sensors [38] as well as MOS based sensors [65].

Figure 6.1. Gas sensor response at 50ºC to H\textsubscript{2} in varying concentrations (10%-100% with 10% increments) with Ar purge between H\textsubscript{2} events [63]. Dashed line represents the n-type Si(001) sensor, and the solid line represents the 3C-SiC sensor. Inset cross-section of 3C-SiC resistive sensor structure.

Figure 6.2. Gas sensor response at 50ºC to H\textsubscript{2} in varying concentrations (10%-100% with 10% increments) without Ar purge between H\textsubscript{2} events.

In order to determine whether the response of the SiC resistive sensors is caused by the adsorption of H\textsubscript{2} on the SiC surface or by the catalytic dissociation of H\textsubscript{2} on the metal surface, the following experiment was performed. New 3C-SiC sensors with ohmic NiCr contacts were fabricated in the same manner discussed previously. In addition to the NiCr ohmic contact, a 100 Å Ti buffer layer followed by an 1800 Å Au layer was deposited by electron beam evaporation. The Ti buffer layer improves the adhesion between the NiCr and Au. It has been reported that gold (Au) is inert to the adsorption of H\textsubscript{2} [18,66]. Thus, the Au layer should prevent a change in electrical properties of the NiCr contact as well as at the NiCr-SiC interface upon adsorption of H\textsubscript{2}. If this assumption is correct the 3C-SiC sensor response to H\textsubscript{2} will only be caused by the adsorption of H\textsubscript{2} on the SiC surface. In addition to using a Au layer, the area between the contacts was also varied while the contact area was kept constant. If the adsorption of H\textsubscript{2} on the SiC surface is the basis of the gas sensing mechanism, an increase in surface area would be expected to generate a larger response.

Two 3C-SiC sensors were fabricated with 1 mm x 3 mm ohmic NiCr/Ti/Au contacts on the same 3C-SiC on Si sample. One sensor had a 0.5 mm gap (1.5 mm\textsuperscript{2} exposed SiC surface) between the contacts whereas the other had a 1 mm gap (3 mm\textsuperscript{2} exposed SiC surface). Both of these sensors showed good linear current versus voltage characteristics
with resistances of approximately 6.7 Ω (1.5 mm² sample) and 6.5 Ω (3 mm² sample). As seen in Figure 6.3, the 3C-SiC sensor with the greater SiC surface area between the contacts (3 mm²) shows a greater response than that of the sensor with the smaller area (1.5 mm²).

![Figure 6.3. Gas sensor response at 50ºC to H₂ in varying concentrations (10%-100% with 10% increments) with Ar purge between H₂ events. Dashed line L = 0.5 mm, solid line L = 1 mm.](image)

The ratio of the response of the SiC sensor with a 3 mm² space between contacts to that of the sensor with a 1.5 mm² space between contacts is expected to be equal to the ratio of the exposed SiC surface area. Doubling the surface area for gas detection would theoretically double the number of adsorption sites available for H₂. A doubling of the possible adsorption sites, assuming the interaction of the adsorption of H₂ is the same everywhere, should double the response of the sensor. The ratio of the responses shown in Figure 6.3 is 1.49 ± 0.05 which is close to the expected value of 2. While this appears to indicate that the sensing mechanism is direct hydrogen adsorption on the exposed 3C-SiC surface, further experimentation is needed to determine the exact gas sensing mechanism of the 3C-SiC resistive hydrogen gas sensors.

### 6.4 Summary

In summary, 3C-SiC resistive hydrogen gas sensors have been fabricated and shown to be capable of detecting hydrogen at concentrations as low at 0.33% in Ar and as high as 100% without any saturation effects seen in other types of gas sensors. These sensors displayed a repeatable response to a continuous change in hydrogen concentration thus indicating that their response is independent of the sensor’s previous environment. Preliminary experiments aimed at determining the gas sensing mechanism for these resistive sensors have been performed and seem to indicate the mechanism is direct hydrogen adsorption on the exposed SiC surface rather than catalytic effects at the metal contacts. Continuing investigation is underway to unlock the specific hydrogen sensing mechanism and to determine the possible impact of gas contaminants on sensor performance.
6.5 Acknowledgements

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Chapter 7: Thermal detection mechanism of SiC based resistive hydrogen gas sensors

Timothy J. Fawcett and John T. Wolan
Chemical Engineering Department, University of South Florida, Tampa, Florida 33620

Anita Lloyd Spetz
S-SENCE and Division of Applied Physics, Linköping University, SE-581 83 Linköping, Sweden

Meralys Reyes and Stephen E. Saddow
Electrical Engineering Department, University of South Florida, Tampa, Florida, 33620


Abstract: Silicon carbide (SiC) resistive gas sensors have been fabricated and tested for sensitivity to hydrogen. Planar NiCr contacts were deposited through SiO$_2$ windows on a 1.4 μm thick 3C-SiC epitaxial film grown on a 15 nm thick Si wafer, which is bonded to a polycrystalline SiC substrate. At 673 K, a resistive gas sensor was shown to detect H$_2$ at concentrations ranging from 1% to 100% H$_2$ in an N$_2$ ambient with up to a 51.75 ± 0.04% decrease in sensor output current from the zero H$_2$ flow baseline value while operating at a maximum power of < 5 mW. The detection mechanism is shown to be caused by a decrease in the device temperature of up to 163.1 ± 0.4 K for 100% H$_2$. This change in device temperature has been shown to be driven by the transfer of heat from the device to the target gas, giving rise to a thermal detection mechanism.

7.1 Introduction

Gas sensors that can operate at high temperatures and in harsh environments are needed for fuel cell [1], aerospace [16], and automotive [3] applications. These applications often require sensor operation at temperatures in excess of 923 K and involve corrosive chemical species such as NO$_x$ [3,16]. Wide bandgap semiconductor materials with excellent chemical and thermal stability, such as silicon carbide (SiC), are being investigated for use in harsh high temperature environments [3,6,7,19-21]. The wide bandgap (2.36 eV for 3C-SiC [67]) allows these materials to operate at elevated temperatures in comparison to silicon whose band gap is only 1.1 eV [13].

Devices based on SiC for gas sensing have included Schottky barrier diodes [9,19-21] and metal-oxide-semiconductor field-effect transistors (MOSFETs) [3,6,7,38], each of which employ a catalytic metal gate to drive their detection mechanisms. Recently, resistive device structures have been investigated for their potential use as gas sensing devices [14,68]. Resistive gas sensors possess several advantages over other sensor device structures including a simplified device fabrication and no catalytic gate metal that
can be poisoned during operation [38]. Also, resistive sensors have demonstrated the ability to detect a wide range of H\textsubscript{2} concentration, from 0.33\% to 100\% H\textsubscript{2} in Ar [14,40,68], a range not seen in catalytic gate Schottky diode or MOSFET sensors [1,6,7,20,21].

7.2 Experimental

Resistive gas sensors were fabricated from a thin 3C-SiC film grown on a 15 nm thick Si wafer, which is bonded to a polycrystalline SiC substrate, referred to as silicon-on-insulator (SOI) in this letter, by a wafer bonding process that is described elsewhere [56]. In this work, a hot-wall SiC chemical vapor deposition (CVD) reactor operating at low pressure was used to grow the 3C-SiC film on the SOI substrate. Details of the 3C-SiC growth process are described elsewhere [58]. The 3C-SiC epitaxial film was measured to have a thickness of 1.4 \( \mu \)m, as determined by FTIR measurement.

After CVD growth a 5000 Å thick SiO\textsubscript{2} layer was deposited on the 3C-SiC surface via plasma enhanced chemical vapor deposition (PECVD). The sensor active areas were then realized by etching windows in the SiO\textsubscript{2} layer followed by the deposition of NiCr (~2000 Å) contacts via \( \varepsilon \)-beam evaporation. These contacts were then rapid thermally annealed for 120 seconds at 1223 K in an Ar ambient to produce contacts with ohmic-like behavior. A Ti (200 Å)/Au (4000 Å) stack was then sputtered on the annealed NiCr to allow for Au wire bonding. Several devices were fabricated on the same die, with contact dimensions of either 0.5 mm x 0.25 m or 0.5 mm x 2 mm and a gap of 0.25 mm between the contacts. A schematic of the device structure is shown in Figure 7.1.

![3C-SiC/SOI resistive device schematic](image)

Devices were then mounted on a Pt-100 resistance temperature detector (RTD) and placed on a ceramic resistive heater. The contacts were then wire bonded to a 16-pin gold package described elsewhere [3]. The packaged sensors were placed in an aluminum plenum housing with each sensor compartment measuring approximately 25.4 mm x 25.4 x 9.5 mm with ~ 4 mm of space for gas to flow over each sensor. The Al housing was connected to a gas manifold system and the gas sensors were tested in various H\textsubscript{2}/N\textsubscript{2} atmospheres. The composition and flow rates of the gases (maintained at a total flow of 100 sccm for all experiments) were digitally controlled via computer-operated mass flow controllers. The resistive gas sensors were tested under a constant dc bias while the current flowing through the sensors was measured by the voltage drop across a precision resistor [69], rated at either a 1 ± 0.02\% or 100 ± 0.005\% \( \Omega \) value, allowing real-time measurement of the sensor resistance via Ohm’s law.
7.3 Results and discussion

Figure 7.2 shows the current flowing through a resistive gas sensor, with 0.5 mm x 0.25 mm contacts and 0.25 mm gap, in response to H₂ exposure from 10% to 100% in a N₂ ambient. The H₂ concentration was varied in 10% increments at an initial device temperature of 673 K while under a constant 10 V dc bias. In this device, the current decreased as H₂ was added to the N₂ ambient with a decrease of up to 51.75 ± 0.04%, calculated from the steady-state portion of the response, from the “baseline” value when pure H₂ was introduced to the gas sensor. The “baseline” is defined as the sensor response to 0% H₂ (i.e., 100% N₂ ambient). The time constant for this device, estimated as a first order exponential decay, was ~ 16 - 22 sec, with the full response occurring at ~90-120 sec after the initial introduction of the gas mixture and is strongly dependent on the H₂ concentration. This response time is a dramatic improvement from our previous reports, where 420-900 sec to full response was not uncommon [14,40,68]. This device demonstrated measurable changes in current of ~1 mA, at H₂ concentrations in a N₂ ambient as low as 1% at 673 K.

In a previous letter [14], we discussed the possibility of the resistive gas sensor response being driven by the adsorption of H₂ on the 3C-SiC surface and its influence on the resistance of the surface. However, new evidence has pointed to thermal effects driving the gas detection. Figure 7.3 shows the temperature of the same device, as measured by the aforementioned RTD in intimate thermal contact with the sensor, while detecting the H₂ pulses whose responses are shown in Figure 7.2. It is clearly seen in Figure 7.3 that the temperature of the device decreases when the sensor is exposed to H₂, with a temperature decrease of up to 163.1 ± 0.4 K when pure H₂ was introduced. It is well known that the resistivity of a semiconductor is strongly temperature dependent [70]. Thus, the temperature decrease, shown in Figure 7.3, causes a change in the
resistivity of the semiconductor material, as seen in the decreasing current shown in Figure 7.2.

Figure 7.3. Measured temperature of a 3C-SiC/SOI resistive gas sensor, with 0.5 mm x 0.25 mm contacts and 0.25 mm gap, in response to 10% to 100% H₂ in N₂ in 10% increments at an initial device temperature of 673 K.

The temperature of the device is governed by the amount of heat transferred from the device to the gas. The heat generated by Joule heating of the resistive gas sensor is transferred to the gas with a magnitude dependent on the thermal properties of gas. This heat transfer can be described by a differential energy balance for a differential unit volume of the device, shown in equation 7.1 [48]:

\[
\frac{\partial}{\partial t} \left( \rho C_p T \right) = \sigma |\nabla V|^2 + k \nabla^2 T
\]

where \( \rho \) is the density, \( C_p \) is the specific heat, \( \sigma \) is the electrical conductivity, \( k \) is the thermal conductivity of the device, and \( V \) and \( T \) are voltage and temperature, respectively. The boundary conditions for this partial differential equation are 1) \( T = T_o \) for \( t = 0 \) at all boundaries and 2) \( q = q_{heater} \) for \( t > 0 \) at the device/heater interface, where \( q \) is heat flux. Newton’s law of cooling defines the heat flux for \( t > 0 \) and for all boundaries except the device/heater interface is shown in equation 7.2 [48]:

\[
q_{surface} = h(T_{gas} - T_{surface})
\]

The energy balance in equation 7.1 does not account for the heat transfer characteristics of the gas, but rather only describes the flow of heat in the device. It is the boundary condition in equation 7.2 that describes the magnitude of heat transferred from the device to the gas (and vice versa). The inlet gas temperature (\( T_{gas} \)) is approximately room temperature (300 K) and is relatively constant (± 2 K) throughout these experiments. Thus, the amount of heat transferred to the gas (\( q_{surface} \)) is related to the temperature of the
surface \( (T_{surface}) \) only through the heat transfer coefficient \( (h) \). It is the heat transfer coefficient that changes with the composition of the gas through the specific heat \( (C_p) \), thermal conductivity \( (k) \), and viscosity \( (\mu) \) of the gas mixture [48] that is responsible for the sensing of gases through a thermal detection mechanism.

The transfer of heat from the device to the gas will occur regardless of which gas and/or gas mixture is flowing over the sensor. However, the magnitude of heat transfer will clearly depend on the thermal properties of the gas. Thus, these sensors actually detect thermal changes relative to a reference gas which is \( \mathrm{N}_2 \) for these experiments. A decrease in temperature upon the introduction of \( \mathrm{H}_2 \), as exhibited in Figure 7.3, suggests that \( \mathrm{H}_2 \) removes more heat from the sensor than \( \mathrm{N}_2 \), a fact that is well known [71], and supported by the thermal properties of \( \mathrm{H}_2 \) \( (k = 0.291 \ \text{W/m·K}, \ C_p = 29.73 \ \text{J/mol·K}) \) relative to \( \mathrm{N}_2 \) \( (k = 0.0041 \ \text{W/m·K}, \ C_p = 29.75 \ \text{J/mol·K}) \) at 600 K [47].

Figure 7.4 shows the mean resistance (as calculated from the measured instantaneous sensor voltage and current) of a resistive gas sensor, with 0.5 mm x 2 mm contacts and 0.25 mm gap, as a function of \( \mathrm{H}_2 \) concentration at 673 K for several gas sensor voltages (2.5 V, 5 V, and 10 V). Increasing gas sensor voltage increases the Joule heating effects (i.e., the \( \sigma \left| \nabla V \right|^2 \) term from equation 7.1) so that more heat is transferred to the gas. With more heat transferred to the gas, the more the device surface temperature \( (T_{surface}) \) will decrease, also shown in Figure 7.3, with a constant heat transfer coefficient, as governed by the boundary condition in equation 7.2. This increased change in temperature results in an increased change in resistance, as demonstrated in Figure 7.4. Thus, the higher the Joule heating, the higher the gas sensor response (i.e., change in resistance).

![Figure 7.4. Calculated resistance (left axis) and measured temperature (right axis) vs. \( \mathrm{H}_2 \) concentration (\( \mathrm{N}_2 \) ambient) for a 3C-SiC/SOI sensor, with 0.5 mm x 2 mm contacts and 0.25 mm gap, at an initial device temperature of 673 K for bias voltages of 2.5, 5, and 10 V DC.](image)

These 3C-SiC resistive gas sensors can be compared to thermistor devices, made primarily from metal oxides such as \( \mathrm{BaTiO}_3 \) [72] and \( \mathrm{SrTiO}_3 \) [73] whose highly temperature dependent resistance is used as a temperature transducer for a variety of applications. Thermistor devices have also been used to indirectly measure heat transfer
coefficients for convective heat transfer [74], similar to those used in the measurements presented in this letter. Thermal conductivity sensors fabricated from materials such as Pt [29] and poly-Si [32] have also been used to measure the thermal conductivity of gas mixtures and for gas detection.

7.4 Summary

In summary, a 3C-SiC/SOI resistive sensor has been fabricated and shown to be capable of detecting H$_2$ over a wide range of concentrations from 10% to 100% H$_2$ in N$_2$, and at a relatively high temperature of 673 K. Initial investigations proposed the dissociation of H$_2$ on the exposed SiC surface, giving rise to a change in surface conductivity, as the gas sensing mechanism [14,40,68]. In contrast to this surface conductivity proposition, this letter provides evidence that the gas sensing mechanism is most likely driven by thermal effects. With the addition of a temperature sensor to the sensor package, the temperature of the sensor was examined while the sensor was exposed to H$_2$. A large change in temperature (up to ~163 K) was observed upon the introduction of pure H$_2$, relative to that in pure N$_2$. This large change in temperature is driven by the transfer of heat from the device (heat that is provided by both the heater and the Joule heating of the resistive sensor) to the gas. Since the resistivity of semiconductor materials is largely dependent on temperature, even small changes in temperature manifest themselves as a significant change in resistivity. This change can be measured electronically and correlated to the concentration of the target gas(es) via the proposed thermal detection mechanism for the 3C-SiC/SOI resistive sensor presented in this study.

7.5 Acknowledgements

This work was supported by the DURINT program administered by the Office of Naval Research (Dr. C. Wood) under Grant N00014-0110715.
Chapter 8: Thermal detection mechanism of 3C-SiC resistive gas sensors

(unpublished data to be submitted to the Journal of Applied Physics)

8.1 Experimental

8.1.1 Device fabrication

In this study, a thin 3C-SiC film was deposited on a silicon-on-insulator (SOI) substrate, diced into a 1 cm x 1 cm die. The SOI substrate consisted of a thin Si (001) layer (~150 Å) miscut 4° towards the [211] direction, bonded to a polycrystalline SiC substrate using a wafer bonding process described elsewhere [56]. The SOI substrate was RCA cleaned prior to deposition to remove trace organic and metal species from the surface [55]. The 3C-SiC deposition was carried out in a low-pressure, hot-wall, horizontal chemical vapor deposition (CVD) reactor using the traditional dual precursor gas chemistry, propane (C\textsubscript{3}H\textsubscript{8}) and silane (SiH\textsubscript{4}) [58]. Hydrogen chloride (HCl) was also incorporated into the gas stream as a growth promoter. During the CVD process a gas stream containing C\textsubscript{3}H\textsubscript{8} and H\textsubscript{2} was established in the chamber while the sample temperature was ramped from room temperature to the growth temperature of 1360°C. Once at the growth temperature, the process pressure was lowered to 200 Torr after which SiH\textsubscript{4} and HCl were added to the gas stream for growth. The Si/C and Si/Cl ratios during growth were set to 0.7 and 3.3, respectively. The 3C-SiC epitaxial film was determined to be ~1.4 μm thick measured via FTIR.

Following deposition of the 3C-SiC epitaxial layer, the sample was RCA cleaned, after which ~5000 Å of silicon dioxide (SiO\textsubscript{2}) was deposited on the surface by plasma-enhanced CVD (PECVD) using SiH\textsubscript{4} and nitrogen dioxide (NO\textsubscript{2}) precursors. Shipley 1813 positive photoresist was used to pattern the SiO\textsubscript{2} layer, to define the active sensor areas, which was subsequently removed using a 10:1 buffered oxide etch (BOE) solution. Next, Futurrex Inc. NR9-1500PY negative photoresist was used to pattern the sample to define the ohmic contact placement. The contacts, ~2000 Å of NiCr (80:20), were deposited via e\textsuperscript{-}-beam evaporation, after which the negative photoresist and undesired NiCr was removed using a standard lift-off process. The sample was rinsed in de-ionized (DI) water, dried in nitrogen (N\textsubscript{2}) and then placed in a rapid thermal processing (RTP) unit to anneal the contacts at 950°C for 2 minutes in an Ar ambient to produce ohmic contacts. After annealing, the NiCr contacts were verified to be ohmic, producing approximately linear current vs. voltage (I-V) characteristics, as demonstrated in Figure 8.1.

Next, another negative photoresist step was performed to pattern the same contact areas previously described; a Ti (200 Å) / Au (4000 Å) stack was sputtered on the existing ohmic contacts to allow for Au wire bonding. The remaining negative photoresist and unwanted Ti/Au was removed using a standard lift-off process. The 1 cm x 1 cm sample was then diced into smaller pieces (~3mm x 6 mm) with each die.
mounted on a resistance temperature detector (RTD) and placed on a ceramic heater with the resistive gas sensor contacts wire bonded to a 16-pin package described elsewhere [3]. A cross sectional drawing of a typical device is shown in Figure 8.2a and a photograph of an actual packaged gas sensor with three devices is shown in Figure 8.2b.

8.1.2 Gas sensor test bed

A schematic drawing of the experimental gas sensor test bed is shown in Figure 8.3. After device fabrication and packaging, the resistive gas sensors were placed in an aluminum (Al) housing connected to a gas manifold system and tested. The composition of the detection gas was controlled by the six mass flow controllers (MFCs) while the timing of the gas mixtures was controlled by pneumatic valves. The resistive gas sensors were tested under a constant dc bias while the current flowing through the sensors was measured by the voltage drop across a precision resistor, either $1 \pm 0.02\%$ or $100 \pm 0.005\% \, \Omega$, allowing the real-time measurement of sensor resistance via Ohm’s law. Ceramic heater and gas sensor bias voltages as well as gas sensor voltage, current and temperature measurements were controlled and collected by an 18-bit multifunction...
analog data acquisition card, PCI-6281 from National Instruments, at a sampling frequency of 10 Hz.

Figure 8.3. Schematic of the experimental gas sensor test bed.

8.2 Results and discussion

8.2.1 Experimental results

The current flowing through a 3C-SiC/SOI resistive gas sensor, with 0.5 mm x 1 mm contacts and a 1 mm gap, in response to 10% to 100% in 10% increments of H$_2$ in N$_2$ with an initial device temperature of 400°C and a 10 Vdc bias is shown in Figure 8.4. The decreases in current shown in Figure 8.4 range from 11.1 ± 0.3 mA or 26.8% (10% H$_2$ in N$_2$) to 34.9 ± 0.2 mA or 84% (100% H$_2$) with time constants, estimated as a first order exponential decay, ranging from ~16-40 seconds. With an RTD in thermal contact with the device, as described in section 8.1.1, the temperature of the device was able to be observed while detecting H$_2$. As demonstrated in Figure 8.5, the temperature of the device decreases as H$_2$ is introduced with magnitudes ranging from 35.9 ± 0.7°C (10% H$_2$ in N$_2$) to 184.1 ± 0.4 °C (100% H$_2$).

As described in section 1.2.2.3, a semiconductor’s resistivity is dependent on temperature. Thus, the temperature changes demonstrated in Figure 8.5 cause the device’s resistivity to change. Since resistance is proportional to resistivity with the proportionality constant being related to the device geometry (as shown in equation 8.1) any changes in resistivity will manifest as changes in resistance for any device with set geometry with cross-sectional area ($A$) and gap length ($L$).

$$R = \rho \frac{L}{A} \quad (8.1)$$
Figure 8.4. Current (left axis) and percent change in current (right axis) flowing through a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to various concentrations (10% to 100% in 10% increments) of H$_2$ in N$_2$ at an initial device temperature of 400°C and a bias of 10 V DC.

Figure 8.5. Temperature of a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to various concentrations (10% to 100% in 10% increments) of H$_2$ in N$_2$ at an initial device temperature of 400°C and a bias of 10 V DC.

The resistance of several 3C-SiC/SOI devices with 0.5 mm x 1 mm contacts, giving a cross-sectional area of ~ 1.4 $\mu$m x 1 mm ~ 1.4·10$^{-9}$ m$^2$, and gap lengths of 0.25 mm, 0.5 mm, and 1 mm is shown in Figure 8.6 as a function of temperature. For all these 3C-SiC/SOI devices, the resistance decreases as temperature increases.

Therefore, the temperature decreases shown in Figure 8.5 cause the device resistance to increase in accordance with Figure 8.6. These resistance increases are recorded as decreases in current at a fixed voltage, as demonstrated in Figure 8.4.
The mean current as a function of H$_2$ concentration for a 3C-SiC/SOI sensor with 0.5 mm x 1 mm contacts with a 1 mm gap for several initial device temperatures, 100°C, 200°C, 300°C and 400°C, with a 10 V DC bias is shown in Figure 8.7. It is clear from Figure 8.7 that this sensor operating at 400°C gives the largest change in current, $\Delta I = 34.9 \pm 0.2$ mA at 100% H$_2$, as already presented in Figure 8.4. It is more appropriate to view the data presented in Figure 8.7 as the percent change in current relative to the baseline (0% H$_2$ or 100% N$_2$), allowing the response to H$_2$ at the four different temperatures to be compared on the same scale. The percent change in current in response to 10% to 100% in 10% increments of H$_2$ in N$_2$ of a 3C-SiC/SOI sensor with 0.5 mm x 1 mm contacts and a gap of 1 mm biased at 10 Vdc is shown in Figure 8.8. It is clear from Figure 8.8 that operating at 400°C gives the largest percent change in current with ~ 84% as previously stated. At H$_2$ concentrations greater than ~ 43.25%, the percent change in current increases with increasing temperature. However, at H$_2$ concentrations less than 43.25% the percent change in current for 200°C operation is greater than that for 300°C operation. The reason for this anomaly is not known and varies as the gap length changes with constant contact dimensions.

The gas sensor resistance is related to the measured current flowing through the sensor at a fixed voltage by Ohm’s law, $R = \frac{V}{I}$. Figure 8.9 shows resistance as a function of H$_2$ concentration for a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, biased at 10 V DC at several temperatures. These resistances correlate to the currents presented in Figure 8.7, with 400°C having the greatest change in resistance, but lowest magnitude. The percent increase in resistance for the same responses shown in Figure 8.9 is shown in Figure 8.10 with up to an ~ 525% increase in resistance at 400°C in response to pure H$_2$. 
Figure 8.9. Resistance as a function of H\textsubscript{2} concentration (in N\textsubscript{2}) of a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, at several initial device temperatures with a bias of 10 V DC.

Figure 8.10. Percent change in resistance of a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, at several initial device temperatures with a bias of 10 V DC.

Figure 8.11 shows the mean resistance as a function of H\textsubscript{2} concentration of a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, at an initial device temperature of 400°C with the sensor biased at several voltages, 2.5V, 5V, and 10V. The change in resistance increases with increasing bias voltage, as demonstrated in Figure 8.11. Increasing gas sensor voltage give increasing Joule heating effects (\(\sigma|\nabla V|^2\) term from equation 1.1) and the ability for more heat to be transferred from the device to the gas. With increased heat transfer comes an increased temperature change for a set heat transfer coefficient, yielding an increasing gas sensor response (change in resistance) as the bias voltage increases.

Figure 8.11. Resistance as a function of H\textsubscript{2} concentration (in N\textsubscript{2}) of a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, at an initial device temperature of 400°C with sensor biased at several voltages.
To test the use of the thermal detection mechanism to explain the gas sensor performance described above, the temperature of the device was controlled using a software proportional-integral-derivative (PID) controller. The temperature was measured using the RTD and controlled using the heater, both described in section 2.2.7. With temperature held constant by the PID controller, the resistance of the device should be constant giving a constant current at a fixed voltage. Figure 8.12 shows the response of a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts and a 1 mm gap, to 10% to 100% in 10% increments of H\textsubscript{2} in N\textsubscript{2} with the device temperature controlled at 400°C. Note, the “spikes” in Figure 8.12 are caused by the PID controller’s compensation for the sudden changes in temperature. Even with temperature controlled at 400°C, the current flowing through the 3C-SiC/SOI sensor is not constant. The current shown in Figure 8.12 increases when H\textsubscript{2} is introduced to the sensor, opposite of when temperature is not controlled.

![Figure 8.12. Current flowing through a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to 10% to 100% H\textsubscript{2} (in N\textsubscript{2}) in 10% increments with device temperature controlled at 400°C and a bias of 10 V DC. Dotted line = H\textsubscript{2} on, dotted line with circle = H\textsubscript{2} off.](image)

The response to H\textsubscript{2} even with the temperature of the device held constant (shown in Figure 8.12) suggests the thermal detection mechanism may not be the only phenomena driving these resistive gas sensor. For example, the adsorption detection mechanism presented in section 1.2.1 may play some part in the overall detection mechanism. However, the sensor was also tested for its response to He diluted in Ar at 100°C, shown in Figure 8.13. Both He and Ar are monatomic noble gases and should react with the gas sensor surface in the same manner. However, He and Ar posses drastically different thermal properties, \( k = 0.0223 \text{ W/m·K} \) and \( C_p = 4.97 \text{ cal/mol·K} \) for Ar and \( k = 0.180 \text{ W/m·K} \) and \( C_p = 4.97 \text{ cal/mol·K} \) for He at 400 K [47]. With the thermal conductivity of He being more than 8 times that of Ar, He can transfer heat at a much faster rate than Ar. Thus, when the concentration of He in a He/Ar mixture increases the heat transfer coefficient of that mixture increases. An increasing heat transfer coefficient lowers the
surface temperature for the same surface heat flux through Newton’s law of cooling,

\[ q_{\text{surface}} = h(T_{\text{gas}} - T_{\text{surface}}) \],

in equation 1.4. Thus the changes in current seen in Figure 8.12 and Figure 8.13 are still the result of heat transfer. Heat is still transferred from the device to the gas, producing a slight temperature gradient in the device, which manifests as changes in current. Experiments testing the sensor response to CO₂ and CH₄ in N₂ while the temperature was controlled were also performed. The device temperature (resistance) decreased (increased) with the exposure of CH₄ and increased (decreased) with the exposure of CO₂. These results are expected with regard to the thermal detection mechanism presented in section 1.2.2. The thermal conductivity of CH₄ (0.0277 W/m·K) is greater than that of N₂ (0.0222 W/m·K), allowing more heat to be transferred from the device to the gas when CH₄ is introduced, causing the device temperature to decrease and resistance to increase. However, the thermal conductivity of CO₂ (0.0129 W/m·K) is less than that of N₂, allowing less heat transferred from the device to the gas, causing the device temperature to increase and resistance to decrease. To completely eliminate heat transfer, the gas must be preheated to exactly the same temperature as the device, a topic addressed in section 9.2.1.

![Figure 8.13](image.png)

Figure 8.13. Current flowing through a 3C-SiC/SOI sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to 10% to 100% He (in Ar) in 10% increments with device temperature controlled at 100°C and a bias of 10 V DC.

### 8.2.2 Finite element method simulations

Finite element method (FEM) simulations, using Femlab 3.2 from COMSOL® [75], were performed to model the thermal and electrical characteristics of a simplified 3C-SiC resistive gas sensor in response to changing H₂ concentrations in N₂ at various initial device temperatures. The details of these simulations are discussed in Appendix C. Figure 8.14 shows the device temperature as a function of H₂ concentration (diluted in N₂) at several initial device temperatures with the sensor biased at 10V DC. As shown in Figure 8.14, the magnitude of the decrease in device temperature increases with increasing initial device temperature.
Figure 8.14. Device temperature as a function of H$_2$ concentration (in N$_2$) at several initial device temperatures. Device biased at 10V DC.

Figure 8.15 shows the simulated resistivity as a function of H$_2$ concentration (in N$_2$) at several initial device temperature with the sensor biased at 10V DC. These resistivity calculations agree with the experimental resistance data presented in Figure 8.9. Figure 8.16 shows the percent change in resistivity as a function of H$_2$ concentration (in N$_2$) at several initial device temperatures. The percent change in resistivity, shown in Figure 8.16 increases with increasing initial device temperature which is in agreement with the experimental result presented in Figure 8.10.

Figure 8.15. Resistivity as a function of H$_2$ concentration (in N$_2$) at several initial device temperatures. Device biased at 10V DC.

Figure 8.16. Percent change in resistivity as a function of H$_2$ concentration (in N$_2$) at several initial device temperatures. Device biased at 10V DC.
Chapter 9: Conclusions and future work

9.1 Conclusions

The detection mechanism driving 3C-SiC resistive hydrogen gas sensors was investigated in this work. Two hypotheses were developed to explain the change in current at a fixed voltage of a resistive device built on a 3C-SiC upon the introduction of different gases to the sensor. The first hypothesis is based on the adsorption of gaseous species on the 3C-SiC surface and subsequent alteration of the semiconductor’s overall conductivity as described in section 1.2.1. Initial experimental data from 3C-SiC/Si resistive sensors, presented in Chapters 5 and 6, suggested the surface adsorption detection mechanism to be responsible for the response of the gas sensors to H$_2$. As the gap length was doubled, with constant contact dimensions, the change in current due to various concentrations of H$_2$ was ~ 1.5 times greater for the device with twice the exposed 3C-SiC surface area. Doubling the surface area doubles the opportunity for H$_2$ to adsorb on the surface and influence the device’s resistance [14]. However, the device temperature was not monitored during these experiments.

The second hypothesis is based on the transfer of heat from the sensor to the gas, causing the temperature of the device to change with changing gas composition as described in section 1.2.2 and termed the thermal detection mechanism. Since a semiconductor’s resistivity is highly temperature dependent, see section 1.2.2.3, any changes in device temperature will manifest a change in resistivity. To experimentally test this hypothesis, a different sensor packaging scheme was employed. The sensor was attached to an RTD (to measure device temperature) and placed on a ceramic heater (to control the device temperature) then placed in a 16-pin Au package (as described in section 2.2.7). As demonstrated in Chapters 7 and 8, the temperature of the device dramatically changes upon the introduction of a different gas mixture to the sensor. A temperature change of up to ~ 184°C upon the introduction of 100% H$_2$ relative to 100% N$_2$ was demonstrated with a 3C-SiC/SOI device operating at an initial temperature of 400°C. This large decrease in temperature caused the 3C-SiC resistivity to increase, resulting in an increase in the observed resistance.

To further test the thermal detection mechanism, the device was operated at various voltages, 2.5 V, 5 V and 10 V, in order to explore the influence the amount of heat generated by the device has on the device performance. Increasing the gas sensor voltage increases the magnitude of the Joule heating term in the energy balance in equation 1.1, allowing more heat to be transferred to the gas at a given initial device temperature. The transfer of more heat from the device to the gas causes the device temperature to decrease due to Newton’s law of cooling for a set heat transfer coefficient (i.e. constant gas composition). The experimental data for two different 3C-SiC/SOI sensors, presented in Figure 7.4 and Figure 8.11, show the change in resistance increasing with increasing bias voltage, providing more evidence to support the thermal detection mechanism hypothesis.
If all temperature changes were eliminated while detecting gases with different heat transfer coefficients, the sensor response should be eliminated if the thermal detection mechanism was solely response for gas detection. However, changes in current at a fixed voltage still occur when H$_2$ is introduced even when the device temperature is held at a fixed value but in the opposite direction than when temperature is not controlled (shown in Figure 8.12). The evidence presented in Figure 8.12 possibly suggest another detection mechanism in addition to the thermal detection mechanism being responsible for the changes in current. However, the same pattern is seen when the same sensor is exposed to He diluted in Ar (shown in Figure 8.13). Both He and Ar have similar chemical reaction characteristics and should influence the device resistance in the same manner if surface adsorption is taking place. Yet, the response to He in Ar (Figure 8.13) follows the same pattern as the response to H$_2$ in N$_2$ (Figure 8.12). Moreover, He and H$_2$ have similar heat transfer characteristics while Ar and N$_2$ also have similar heat transfer characteristics, see Table 1.1. Thus, the thermal effects of detecting He in Ar are approximately the same as those when detecting H$_2$ in N$_2$. Also, heat transfer still occurs even while the temperature of the device is held constant by a PID controller since the gas enters the sensor housing at approximately room temperature. This small amount of heat transfer is most likely responsible for the small changes in current found in Figure 8.12 and Figure 8.13.

Thus, the evidence presented in Chapters 7 and 8 supports that gas sensing is being driven by the thermal detection mechanism. The large changes in temperature upon the introduction of a gas with different heat transfer characteristics than the reference gas cause corresponding changes in the device resistance. In effect, any gas mixture made up of gases with different thermal properties will produce a response in 3C-SiC resistive gas sensors. Thus, instead of a H$_2$ specific gas sensor, these 3C-SiC sensors can detect any gases that have different thermal properties. For example, H$_2$ can be detected in any gas other than He since the thermal properties of He are very close to that of H$_2$. CO$_2$ can also be detected in N$_2$ or H$_2$ since the thermal properties of CO$_2$ are different than those of both N$_2$ and H$_2$.

These changes in resistance are measured as changes in current at a fixed voltage. The influence of the gas sensor bias voltage on the magnitude of the change in resistance, due to the Joule heating’s dependence on voltage, also supports the thermal detection mechanism being responsible for the gas sensing. Although small changes in current where demonstrated even with the temperature of the device held constant, the thermal detection mechanism is still the mostly likely explanation for the detection mechanism of wide bandgap resistive gas sensors.

Finite element method (FEM) simulations, presented in section 8.2.2, have confirmed many of the experimental findings presented in Chapters 7 and 8. The device temperature was shown to decrease with increasing H$_2$ concentration in N$_2$. The magnitude of the decrease in device temperature increased with increasing initial device temperature. Both of these simulated results agree with the experimental trends presented in Chapters 7 and 8. Thus, the experimental and theoretical evidence presented in this work support the thermal detection mechanism as being the main driving force for the detection of H$_2$ by 3C-SiC/SOI resistive gas sensors.
9.2 Future work

9.2.1 Further investigation into the thermal detection mechanism for resistive sensors

Preheating the gas inlet to the same temperature as the resistive gas sensor will eliminate any temperature gradients in the system and therefore eliminate any transfer of heat from the device to the gas. Thus, preheating the gas should essentially eliminate the possibility of gas detection via thermal effects. If a gas sensor response still arises upon the introduction of a gas or gas mixture with different thermal properties, the thermal detection mechanism is not the only mechanism responsible for the response of these 3C-SiC resistive gas sensors.

Varying the total gas flow over the sensor can also give further proof to the thermal detection mechanism. Changing the total gas flow will also change the heat transfer coefficient, through the Reynolds number as discussed in section C.4. For example, if adjusting the total flow of pure $\text{N}_2$ to obtain the same heat transfer coefficient as pure $\text{H}_2$ yields the same sensor response, the thermal detection mechanism is the main driving force for $\text{H}_2$ detection.

9.2.2 Improved gas sensor performance

Optimization of the gas sensor device structure has yet to be ascertained. The goal of this work was to understand the detection mechanism using different device geometries. With the gas sensor detection mechanism most likely being thermal in nature, device structures can be optimized. For example, as stated in section 1.2.2.3, lightly doped SiC yields a much larger temperature coefficient of resistance compared to highly doped SiC. Thus, a more sensitive sensor can be realized with using a very lightly doped substrate. Factors such as doping and device dimensions should be fully characterized to determine the optimum sensor parameters.

9.2.3 Test resistive sensor sensitivity to other gases

The sensitivity of 3C-SiC resistive sensors to other gases must also be thoroughly explored. This report investigated the sensitivity of 3C-SiC resistive sensors to $\text{H}_2$ in Ar and $\text{N}_2$ in order to ascertain the detection mechanism. With the thermal detection mechanism driving the gas sensor response, other gas mixtures should be able to be detected as long as differences in thermal properties exists.

9.2.4 On device temperature measurement

The device temperature for the second generation devices described in section 2.2 is measured by a RTD located direction beneath the device. The device and RTD are in intimate thermal contact with a high thermal conductivity epoxy connecting them. This temperature measurement can be improved if the temperature measuring structure was either directly on the device, without the epoxy layer, or in the device. The deposition of a standard Pt film, with known resistance and temperature coefficient of resistance, directly on the device surface will give a better indication of temperature. With the Pt RTD directly on the device the epoxy layer is eliminated, giving a better indication of temperature.
References


http://www.dupont.com/kapton/.


[69] Available from Precision Resistor Company, Inc.


Appendices
Appendix A. Derivation of heat transfer equations

Table A.1. Notation for derivation of heat transfer equations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
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<td>sec</td>
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<tr>
<td>$\rho$</td>
<td>density</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>magnitude of velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$\hat{H}$</td>
<td>enthalpy</td>
<td>J/kg</td>
</tr>
<tr>
<td>$Q_{\text{source}}$</td>
<td>source of heat</td>
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</tr>
<tr>
<td>$e$</td>
<td>combined energy flux vector</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>velocity vector</td>
<td>m/s</td>
</tr>
<tr>
<td>$g$</td>
<td>gravity vector</td>
<td>m/s$^2$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat or heat capacity</td>
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</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\dot{j}$</td>
<td>current density vector</td>
<td>A/m$^2$</td>
</tr>
<tr>
<td>$E$</td>
<td>electric field vector</td>
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<td>$\sigma$</td>
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<td>$V$</td>
<td>voltage</td>
<td>V</td>
</tr>
<tr>
<td>$\tau$</td>
<td>viscous momentum-flux tensor</td>
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</tr>
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<td>$q$</td>
<td>heat flux by molecular conduction</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity</td>
<td>W/m·K</td>
</tr>
<tr>
<td>$T_o$</td>
<td>Initial temperature</td>
<td>K</td>
</tr>
<tr>
<td>$q_{\text{heater/device}}$</td>
<td>heat flux at the heater/device interface</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$q_{\text{heater}}$</td>
<td>heat flux generate by the heater</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$q_{\text{surface}}$</td>
<td>heat flux at all surfaces except heater/device interface</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$h$</td>
<td>heat transfer coefficient</td>
<td>W/m$^2$·K</td>
</tr>
<tr>
<td>$T_{\text{gas}}$</td>
<td>bulk temperature of the gas</td>
<td>K</td>
</tr>
<tr>
<td>$T_{\text{surface}}$</td>
<td>temperature at the surface</td>
<td>K</td>
</tr>
</tbody>
</table>

The general differential energy balance on a differential volume unit, including a source of heat, is shown in equation A.1, adapted from [48].

$$\frac{\partial}{\partial t} \left( \rho \nu \hat{v} + \rho \hat{H} \right) = Q_{\text{source}} - (\nabla \cdot e) + \rho (\nu \cdot g)$$  \hspace{1cm} (A.1)

The term on the left-hand-side of the equation represents the rate of increase of energy per unit volume and consists of a kinetic energy and an enthalpy term, reading from left to right. In the gas sensor problem at hand, the device is not moving, thus velocity is zero.
Appendix A (Continued)

everywhere and for all times, leaving only the enthalpy term. The enthalpy can be related
to temperature through the thermodynamic definition of specific heat [76], given in
equation A.2.

\[ C_p \equiv \frac{\partial \hat{H}}{\partial T} \]  

(A.2)

The definition of specific heat given in equation A.2 must be manipulated to fit the form
needed for the differential balance in equation A.1. This slight manipulation, taking the
time derivative, is shown in equation A.3.

\[ d\hat{H} = C_p dT \quad \therefore \quad \frac{\partial}{\partial t} (d\hat{H}) = \frac{\partial}{\partial t} (C_p dT) \]  

(A.3)

After the manipulations given above, the left-hand-side of equation A.1 reduces to the
expression found in equation A.4.

\[ \frac{\partial}{\partial t} \left( \frac{1}{2} \rho \nu^2 + \rho \hat{H} \right) = \frac{\partial}{\partial t} \left( \frac{1}{2} \rho \nu^2 \right) + \frac{\partial}{\partial t} \left( \rho \hat{H} \right) = 0 + \frac{\partial}{\partial t} \left( \rho C_p dT \right) \]  

(A.4)

The first term in the right-hand-side of the differential energy balance, equation A.1, is the heat source term. In the gas sensor problem, the heat source is the Joule heating of the device due to current flowing through the device. The derivation of this term starts with the definition of Joule heating, shown in is shown in equation A.5 [77].

\[ Q_{source} = j \cdot E \]  

(A.5)

\[ j = \sigma E \]  

(A.6)

\[ E = \nabla V \]  

(A.7)

The definition of Ohm’s Law (equation A.6) [70] and electric field (equation A.7) are substituted into equation A.5 to yield a useful Joule heating term shown in A.8.

\[ Q_{source} = j \cdot E = (\sigma E) \cdot E = \sigma |E|^2 = \sigma |\nabla V|^2 \]  

(A.8)
Appendix A (Continued)

The second term in the right hand side of equation A.1 contains the combined energy flux vector and can be expanded into three terms, including 1) convective transport, 2) rate of molecular done, and 3) rate of conduction by molecular means, shown in equation A.9 [48].

\[
\varepsilon = \left( \frac{1}{2} \rho v^2 + \rho \dot{H} \right) v + \left[ \varepsilon \cdot v \right] + q 
\]  

(A.9)

The first and second terms in equation A.9, the convective heat transfer term and molecular work term respectively, will both equal zero since the device is not moving and has a velocity of zero. The third term in equation A.9 is the heat conduction term, and is defined by Fourier’s Law, shown in equation A.10 [48].

\[
q = -k \nabla T 
\]  

(A.10)

Substituting equation A.10 into the second term of the right hand side of equation A.1 yields equation A.11.

\[
\varepsilon = \left( \frac{1}{2} \rho v^2 + \rho \dot{H} \right) v + \left[ \varepsilon \cdot v \right] + q = 0 + 0 - k \nabla T \\
\nabla \cdot \varepsilon = \nabla \cdot ( - k \nabla T ) = -k \nabla T^2 \\
\nabla \cdot \varepsilon = -k \nabla T^2 
\]  

(A.11)

The last term on the right hand side of equation A.1 evaluates to zero since the device is not moving and has zero velocity, shown in equation A.12.

\[
\rho \left( \nabla \cdot \dot{g} \right) = 0 
\]  

(A.12)

Substituting equations A.4, A.8, A.11, and A.12 into the differential energy balance in equation A.1 yields equation A.13, the final form of the differential energy balance.

\[
\frac{\partial}{\partial t} \left( \rho C_p T \right) = \sigma |\nabla V|^2 + k \nabla^2 T 
\]  

(A.13)

To completely define the heat transfer problem, boundary conditions must be specified along with the differential energy balance in equation A.13. The initial condition, a Dirichlet condition, for this problem is specified in equation A.14. The second boundary condition, a Neumann condition, specifies the heat flux from the heater as being equal to the heat flux through the heater/device interface, as specified in equation A.15.

\[
T = T_o \\
t = 0, \text{ everywhere} 
\]  

(A.14)
Appendix A (Continued)

\[ q_{\text{heater/device}}^| = q_{\text{heater}} = -k\nabla T_{\text{heater/device}} \]
\[ t > 0, \text{ heater/device interface} \]

The final boundary condition, also a Neumann condition, specifies the heat flux from all surfaces of the device with the exception of the heater/device interface, specified in equation A.16.

\[ q_{\text{surface}} = h(T_{\text{gas}} - T_{\text{surface}}) = q_{\text{surface}} = -k\nabla T_{\text{surface}} \]
\[ t > 0, \text{ all surfaces except heater/device interface} \]

At all surfaces associated with this final boundary condition, heat is transferred from the surface to the gas by convection with a magnitude described by Newton’s law of cooling [48]. It is convection that provides the means of transferring energy from the device to the gas, with Newton’s law being the general model. Thus, the heat transfer coefficient \( h \) is the property of the gas or gas mixture that is being detected when the thermal detection mechanism is responsible for the gas sensing mechanism.
Appendix B. Derivation of temperature dependence of carrier concentrations

Table B.1. Notation for derivation of temperature dependence of carrier concentrations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>concentration of electronics in conduction band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$p$</td>
<td>concentration of holes in valence band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$E$</td>
<td>energy</td>
<td>eV</td>
</tr>
<tr>
<td>$g(E)$</td>
<td>density of states (general)</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>$\hbar = h/2\pi$</td>
<td>J·s</td>
</tr>
<tr>
<td>$H$</td>
<td>Plank’s constant $= 6.63 \cdot 10^{-34}$ J·s</td>
<td>J·s</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass</td>
<td>kg</td>
</tr>
<tr>
<td>$f(E)$</td>
<td>Fermi function</td>
<td>ratio</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi level</td>
<td>eV</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant $= 8.614 \cdot 10^{-5}$ eV/K</td>
<td>eV/K</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$g_c(E)$</td>
<td>density of states in the conduction band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$E_c$</td>
<td>conduction band edge</td>
<td>eV</td>
</tr>
<tr>
<td>$g_v(E)$</td>
<td>density of states in the valence band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$E_v$</td>
<td>valence band edge</td>
<td>eV</td>
</tr>
<tr>
<td>$m_e$</td>
<td>mass of electron</td>
<td>kg</td>
</tr>
<tr>
<td>$m_h$</td>
<td>mass of hole</td>
<td>kg</td>
</tr>
<tr>
<td>$E_g$</td>
<td>bandgap $=</td>
<td>E_c - E_v</td>
</tr>
<tr>
<td>$N_c$</td>
<td>effective density of states in the conduction band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$N_v$</td>
<td>effective density of states in the valence band</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$n_i$</td>
<td>intrinsic carrier concentration</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$N_D^+$</td>
<td>concentration of ionized donors</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$N_A^-$</td>
<td>concentration of ionized acceptors</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$g_D$</td>
<td>Donor degeneracy factor</td>
<td></td>
</tr>
<tr>
<td>$E_D$</td>
<td>Donor energy level</td>
<td>eV</td>
</tr>
<tr>
<td>$g_A$</td>
<td>acceptor degeneracy factor</td>
<td></td>
</tr>
<tr>
<td>$E_A$</td>
<td>acceptor energy level</td>
<td>eV</td>
</tr>
<tr>
<td>$q$</td>
<td>magnitude of an electronic charge $= 1.60 \cdot 10^{-19}$</td>
<td>C</td>
</tr>
</tbody>
</table>

The number of electrons ($n$) and holes ($p$) per cubic unit volume of semiconductor material having an energy between $E$ and $E + dE$ is given by the density of states, $g(E)$, where the density of states is given in equation B.1 without derivation [78].

$$g(E) = \frac{V}{2\pi^2 \hbar^3} (2m)^{3/2} E^{3/2}$$

(B.1)
Appendix B (Continued)

The probability density function that gives the ratio of the filled energy states to the total allowed energy states of a particle at a given energy is the Fermi function, \( f(E) \), given in equation B.2 also without derivation [51].

\[
f(E) = \frac{1}{1 + e^{(E-E_F)/k_B T}} \quad \text{(B.2)}
\]

This, the total number of carriers in the conduction (electrons) and valence (holes) bands of a semiconductor is found by integrating the total number of filled states, given by multiplying the total number of possible states, the density of states \( g(E) \), by the fraction of those states that are occupied at a given energy, \( f(E) \). This integration is displayed in equation B.3 with density of states shown in equation B.4 [51].

\[
n = \frac{1}{V} \int_{E_c}^{\infty} g_c(E) f(E) \, dE \\
p = \frac{1}{V} \int_{-\infty}^{E_v} g_v(E) [1 - f(E)] \, dE
\]

\[
g_c(E) = \frac{V}{2\pi^2 h^3} (2m_e)^{3/2} E^{3/2} \quad \text{(B.3)}
\]

\[
g_v(E) = \frac{V}{2\pi^2 h^3} (2m_h)^{3/2} E^{3/2} \quad \text{(B.4)}
\]

The Fermi function in equation B.2 can be simplified under the assumption that the Fermi is in the band gap, \( E_g \), and more than \( 3k_B T \) from either band edge. Under this assumption, the Fermi function becomes expressed by equation B.5 [51,78].

\[
f(E) \approx e^{(E-E_F)/k_B T} \quad \text{(B.5)}
\]

Substitution and manipulation of the conduction band density of states from equation B.4 and the modified Fermi function from equation B.5 into the electron concentration equation, B.3, yields the electron concentration given in equation B.6. A similar process is used to calculate the hole concentration, given in equation B.7 [51,78].

\[
n = \frac{1}{V} \int_{E_c}^{\infty} g_c(E) f(E) \, dE = \frac{1}{V} \int_{E_c}^{\infty} \frac{V}{2\pi^2 h^3} (2m_e)^{3/2} E^{3/2} e^{(E-E_F)/k_B T} \, dE \\
= \frac{(2m_e)^{3/2}}{2\pi^2 h^3} e^{E_F/k_B T} \int_{E_c}^{\infty} E^{3/2} e^{-E/k_B T} \, dE \\
= 2\left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2} e^{(E_F-E_c)/k_B T} = N_e e^{(E_F-E_c)/k_B T} \quad \text{(B.6)}
\]

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Appendix B (Continued)

\[ p = 2 \left( \frac{2\pi n_i k_B T}{h^2} \right)^{\frac{3}{2}} e^{(E_v - E_F)/k_B T} = N_c e^{(E_v - E_F)/k_B T} \quad (B.7) \]

For a semiconductor with no impurities, charge neutrality must be maintained, giving rise to the law of mass action definition of the intrinsic carrier concentration given in equation B.8 [51].

\[ n_i^2 = np = \left( N_c e^{(E_v - E_F)/k_B T} \right) \left( N_p e^{(E_v - E_F)/k_B T} \right) = N_c N_p e^{(E_v - E_F)/k_B T} \quad (B.8) \]

The electron and hole concentrations given by equations B.6 and B.7 only account for the carriers associated with the intrinsic semiconductor atoms and not for impurity atoms (donors or acceptors). For an impurity atom to be able to transport charge, and act as a carrier, it must be ionized, i.e. a donor must be willing to give up an electron. The fraction of donor and acceptor atoms that are ionized is given in equations B.9 and B.10 respectively [51].

\[ N_D^+ = \frac{1}{1 + g_D e^{(E_F - E_D)/k_B T}} \quad (B.9) \]

\[ N_A^- = \frac{1}{1 + g_A e^{(E_A - E_F)/k_B T}} \quad (B.10) \]

A total charge balance within the semiconductor is shown in equation B.11 [51].

\[ p - n + N_D^+ - N_A^- = 0 \]

\[ N_c e^{(E_v - E_F)/k_B T} - N_c e^{(E_v - E_F)/k_B T} \frac{N_D}{1 + g_D e^{(E_F - E_D)/k_B T}} - \frac{N_A}{1 + g_A e^{(E_A - E_F)/k_B T}} = 0 \quad (B.11) \]
Appendix C. Details of finite element method simulations

C.1 Geometry

Finite element method (FEM) simulations were performed on a simplified 3C-SiC resistive device using Femlab 3.2 from COMSOL®. The simulation utilized the “Conductive Media DC” and “Heat Transfer by Conduction” modules [75] with a geometry consisted of a 1 cm x 1 cm x 300 μm solid sample with 0.2 cm x 1 cm contacts, as shown in Figure C.1.

![Device simulation geometry.](image)

Figure C.1. Device simulation geometry.

C.2 Governing equations

The governing equation for the “Conductive Media DC” module is a charge balance on a differential volume of the device which includes electron conduction ($\sigma \nabla V$), external current sources ($J_e$) and internal current sources ($Q_j$), shown in equation C.1 [75].

$$- \nabla \cdot (\sigma \nabla V - J_e) = Q_j$$

Equation C.2 shows the general energy balance equation on a differential volume of the device [75]. See 0 for a detailed derivation of this equation.

$$\delta_n \rho C_p \frac{\partial T}{\partial t} - \nabla \cdot (k \nabla T) = Q$$

C.3 Subdomain properties

The subdomain properties are the properties of the substance(s) in the simulation. For the “Heat Transfer by Conduction” module, the built-in thermal properties of SiC, thermal conductivity = 490 W/(m·K), density = 3216 kg/m$^3$, and heat capacity = 690 J/(kg·K) were used. For the “Conductive Media DC” module, the resistivity of 3C-SiC was estimated using the resistance versus temperature data from a 3C-SiC/SOI device, as described below.
Appendix C (Continued)

The resistance versus temperature data from a 3C-SiC/SOI device with 0.5 mm x 1 mm contacts with a 1 mm gap was used to estimate the resistivity of the 3C-SiC epitaxial layer using equation C.3 where \( R(T) \) is the device resistance, \( \rho(T) \) is the resistivity, \( L \) is the gap length and \( A \) is the cross-sectional area (epi-layer thickness x contact width).

\[
R(T) = \rho(T) \frac{L}{A} \Rightarrow \rho(T) = R(T) \frac{A}{L}
\]  

(C.3)

The resistance versus temperature characteristics of this device are shown in Figure 8.6 while the resistivity versus temperature characteristics of this device are shown in Figure C.2. The exponential relationship between resistivity and temperature was then extracted using standard linear regression to produce the relationships given in equation C.4.

\[
\ln \rho = -0.0108T - 0.7491
\]

\[
\rho = 0.4728e^{-0.0108T}, \theta = \text{[\text{\Omega m}]}, T = \text{[\text{K}]}
\]  

(C.4)

![Figure C.2](image)

Figure C.2. Resistivity versus temperature of a 3C-SiC/SOI resistive gas sensor with 0.5 mm x 1 mm contacts with a 1 mm gap.

C.4 Boundary conditions

There are eight boundaries that require boundary conditions in this simulation. There are three boundaries on the “top” of the device, two contacts and the exposed, or active, area, four sides of the device each give a boundary, and one boundary on the bottom of the device. Thus, eight boundary conditions are required for both the “Conductive Media DC” and “Heat Transfer by Conduction” modules.

For the “Conductive Media DC” module, a voltage is applied to one of the contacts while the other contact is held at ground while all other boundaries are electrically isolated. For the “Heat Transfer by Conduction” module, the bottom of the device has a specified heat flux (termed the heat flux from the heater) while all heat flux from all other boundaries is specified by Newton’s Law of Cooling, shown in equation C.5, where
Appendix C (Continued)

\( q_{\text{surface}} \) is the heat flux from the surface, \( h \) is the heat transfer coefficient, \( T_{\text{gas}} \) is the temperature of the gas and \( T_{\text{surface}} \) is the temperature of the surface.

\[
q_{\text{surface}} = h(T_{\text{gas}} - T_{\text{surface}})
\]  

(C.5)

The heat transfer coefficient can be estimated using an empirical relationship, shown in equation C.6, relating the Nusselt number (\( Nu \)) to the Prandtl number (\( Pr \)) and Reynolds number (\( Re \)) for convective heat transfer over flat plates [47, 79, 80].

\[
Nu = 0.664 Pr^{1/3} Re^{1/2}
\]  

(C.6)

The definitions of \( Nu \), \( Pr \) and \( Re \), are presented in equation C.7 where \( h \) is the heat transfer coefficient, \( L \) is the characteristic length, \( k \) is the thermal conductivity, \( \mu \) is the viscosity, \( C_p \) is the heat capacity, \( \rho \) is the density and \( v_{\text{gas}} \) is the velocity of the gas.

\[
Nu = \frac{hL}{k}, \quad Pr = \frac{\mu C_p}{k}, \quad Re = \frac{\rho v_{\text{gas}} L}{\mu}
\]  

(C.7)

The gas properties were taken from the National Institute of Standards and Technology (NIST) Chemistry WebBook, Standard Reference Database 69 [81]. For a specific gas, \( \text{H}_2 \) or \( \text{N}_2 \) in these simulations, the \( Pr \) and \( Re \) can be calculated. Thus, through equation C.6, \( Nu \) can be calculated and \( h \) extracted using the definition of \( Nu \) in equation C.7.

**C.5 Simulation procedure**

With a contact gas composition, the bias voltage and heat flux from the heater determine the device temperature. Figure C.3 shows a “slice” plot from a device biased at 10V DC with the heat flux from the heater being 117.8351 W/m\(^2\) to give a device temperature of 373.15 K (or 100°C) and pure \( \text{N}_2 \) making up the heat transfer coefficient (1.4 W/m\(^2\)·K). Under pure \( \text{N}_2 \) conditions, the device temperature was determined at various values of the heat flux from the heater (\( Q \)) to determine the heat flux needed to obtain initial device temperatures of 373, 473, 573, and 673 K, shown in Figure C.4. Thus, the heat flux from the heater is chosen according to the desired initial device temperature using the relationship in Figure C.4. The heat transfer coefficient is then swept from its pure \( \text{N}_2 \) value of ~ 1.4 W/m\(^2\)·K to its pure \( \text{H}_2 \) value of ~ 1.6 W/m\(^2\)·K with the heat flux from the heat constant. The equations governing heat transfer and DC conduction equations, presented in section C.2, are then solved using the boundary conditions specified in section C.4. The results of these simulations are presented and discussed in section 8.2.2.
Figure C.3. Device temperature under pure N\textsubscript{2} at 373 K. Device biased at 10V DC.

Figure C.4. Device temperature as a function of heater heat flux. Device biased at 10V DC.
About the Author

Timothy J. Fawcett received his Bachelor of Science and Master of Science degrees in Chemical Engineering from the University of South Florida in May 2004 where his research explored the potential application of SiC based resistive devices as hydrogen gas sensors. He has been pursuing his Doctor of Philosophy degree in Chemical Engineering since that time and has been active in the SiC community with his research focused on understanding the gas sensing mechanism driving SiC based resistive gas sensors. Timothy has published several peer-reviewed journal articles in addition to presenting his gas sensor research at several conferences. After graduation, Dr. Fawcett plans to continue SiC based gas sensor research at the University of South Florida.