Silicon Carbide Micro-devices for Combustion Gas Sensing under Harsh Conditions

Final Technical Report

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ABSTRACT

A sensor based on the wide bandgap semiconductor, silicon carbide (SiC), has been developed for the detection of combustion products in power plant environments. The sensor is a catalytic gate field effect device, Pt/SiO₂/SiC that can detect hydrogen-containing species in chemically reactive, high temperature (600 °C) environments.

We demonstrate that the device can be used as a hydrogen monitor in syngas applications of common interferants as well as sulfur and water vapor. These measurements were made in the Catalyst Screening Unit at NETL, Morgantown under atmospheric conditions. The sensor response to hydrogen gas at 350 °C is 240 mV/decade, this is significantly higher than the device response to room temperature gas or that predicted from vacuum chamber studies. The enhanced catalytic activity of the platinum sensing film under energy plant operating conditions was investigated via AFM, x-ray diffraction, TEM and x-ray photoelectron spectroscopy. Our characterization indicated that exposure to high temperature gases significantly modifies the morphology of the Pt catalytic film and the Pt/SiO₂ interfacial region, which we tentatively attribute to the enhanced hydrogen sensitivity of the sensing film. A model for the hydrogen/oxygen response of the SiC device under atmospheric conditions was developed. It is based on two independent phenomena: a chemically induced shift in the metal-semiconductor work function difference and the passivation /creation of charged states at the SiO₂-SiC interface. The optimum operating set point for the SiC sensor with respect to response time and long term reliability was determined to be close to mid-gap.

Ultrahigh vacuum (UHV) techniques were used to investigate the effects of sulfur contamination on the Pt gate. Exposure to hydrogen sulfide, even in the presence of hydrogen or oxygen at partial pressures of 20-600 times greater than the H₂S level, rapidly coated the gate with a monolayer of sulfur. Although hydrogen exposure could not remove the adsorbed sulfur, oxygen was effective at removing sulfur with no evidence of irreversible changes in device behavior. The role of oxygen in the functioning of the SiC sensors was also investigated. All of the results are consistent with oxygen acting through its surface reactions with hydrogen, including the need for oxygen to reset the device to a fully hydrogen-depleted state and competition between hydrogen oxidation and hydrogen diffusion to metal/oxide interface sites. A strong sensor response to the unsaturated linear hydrocarbon propene (C₃H₆) was observed.

TABLE OF CONTENTS

DISCLAIMER	2
ABSTRACT.....	3
LIST(S) OF GRAPHICAL MATERIALS	5
LIST(S) OF TABLES.....	6
1. INTRODUCTION.....	7
2. EXECUTIVE SUMMARY	9
3. EXPERIMENTAL	17
3.1 <i>Sensor fabrication, activation and characterization</i>	17
3.2 <i>Photoemission measurement technique</i>	18
3.3 <i>Sensor measurements in an “industrial” reactors at NETL, Morgantown, WV</i> 19	
3.4 <i>Pt film characterization</i>	23
3.5 <i>Ultrahigh vacuum measurements</i>	24
4. RESULTS AND DISCUSSION.....	30
4.1 <i>High Temperature Oxide Reliability</i>	30
4.2 <i>Time Resolved Sensor Measurements</i>	32
4.3 <i>UHV Measurements of Sensor Response</i>	34
4.4 <i>UHV Sensitivity to hydrocarbons (propene) and CO</i>	35
4.5.1 <i>UHV studies of sulfur surface chemistry on the Pt gate</i>	39
4.6 <i>Industrial Sensor Measurements</i>	44
4.7 <i>Effect of activation and high temperature gas on sensor morphology and</i> <i>structure</i>	55
5. CONCLUSION	66
ACKNOWLEDGEMENTS	67
REFERENCES.....	68
BIBLIOGRAPHY	72
LIST OF ACRONYMS AND ABBREVIATIONS.....	73

LIST(S) OF GRAPHICAL MATERIALS

Fig. 1.1 Schematic of a SiC field-effect sensor for H ₂ -containing gases	7
Fig. 1.2. High frequency(1MHz) C-V characteristic of a SiC sensor	8
Fig. 3.1.1 Photograph of the inside of the test module showing SiC sensor chip.	17
Fig. 3.2.1 Schematic of the set-up for photoemission measurements	18
Fig. 3.3.1..Photograph of SiC sensor test module installed in the micro-reactor	19
Fig. 3.3.2 SiC sensor test “team”: from NETL - Dr. Benjamin Chorpening	20
Fig. 3.3.3 Photograph of the setup for both thermometry and sensor measurements	22
Fig. 3.5.1. Schematic diagram of the electrostatic shield and negatively	25
Fig. 3.5.2. Pressure-time traces measured by the QMS during sample heating	26
Fig. 3.5.3 UHV sample mount. The ring with keyhole slots is the sample	27
Fig. 3.5.4. Calibration of RGA signal against actual pressure for hydrogen	28
Fig. 3.5.5. Front panel of the constant-temperature PID control program.	29
Fig. 4.1. Gate leakage current density as a function of temperature for 6H-SiC	30
Fig. 4.2.1: Schematic of the fast gas sensor measurement apparatus	32
Fig. 4.2.2: Schematic of the laser induced fluorescence images of the MGO (a)	33
Fig. 4.3.1. Sensor response in UHV to varying hydrogen pressure	34
Fig. 4.4.1 UHV response of Gate #83 to a) hydrogen and b) propene (C ₃ H ₆)	35
Fig. 4.4.2. Sensor response in UHV to varying propene pressure in the presence	36
Fig. 4.4.3. Auger spectra of the Pt gate after cleaning, after exposure	37
Fig. 4.4.4 Attempt to measured sensor response to carbon monoxide, on Gate #41	38
Fig. 4.5.1. Normalized sticking coefficient of sulfur from H ₂ S as a function of	40
Fig. 4.5.2. Comparison of Auger signals from clean and sulfur-contaminated Pt	41
Fig. 4.5.3. Reaction coefficient (S atoms removed per incident O ₂ molecule) for	43
Fig. 4.6.1 Sensor sensitivity (ΔV) as a function of hydrogen concentration from a	44
Fig. 4.6.2. Validation of the SiC hydrogen sensor measurements with mass	45
Fig. 4.6.3 Hydrogen sensor performance under “typical” fuel reforming	46
Fig.4.6.4 Performance of the SiC sensor under “typical” fuel reforming	48
Fig.4.6.5 Performance of the SiC sensor in a “typical” fuel reforming	49
Fig. 4.6.6. Sensor sensitivity before and after exposure to H ₂ S as a function of	51
Fig. 4.6.7 Photograph of the sensor chip (a) and the chip mounted in module #1 (b)	52
Fig. 4.6.8 Photographs of the sensor chip and holder after 8 days of measurement	52
Fig. 4.6.9. Sensor sensitivity as a function of hydrogen concentration for a	53
Fig. 4.7.1 I ² R heater power required to maintain the Pt sensing film at 600	55
Fig. 4.7.2. High magnification micrographs of a few Pt gates before activation.	57
Fig. 4.7.3. A bright field image of a device before activation.	58
Fig. 4.7.4. AFM images of a 1000 μ m Pt gate of an as grown sample .	59
Fig. 4.7.5 Pt 4f image of a 1000 μ m diameter sensing film	60
Fig. 4.7.6 Sputter depth profiling of a sensing film following extended testing in	61
Fig. 4.7.7 X-ray diffraction scans of Pt sensing layers deposited on oxidized SiC	62
Fig. 4.7.8 X-ray diffraction scans of Pt sensing layers deposited on oxidized SiC	63
Fig. 4.7.8. TEM-cross sectional viewgraph of “As Grown sample”.	64
Fig. 4.7.9. TEM-cross sectional viewgraph of “Sample Operated in Industrial	65

LIST(S) OF TABLES

Table 4.6.1 lists the typical stream composition from: (i) the Cold-Gas Clean-up	47
Table 4.6.2 H ₂ S levels for the data in Fig. 4.2.3.2 (for 11/1/06)	49
Table 4.7.1 lists the typical stream composition from: (i) the Cold-Gas Clean-up	56
Table 4.7.2 X-ray diffraction parameter for Pt, PtO and PtO ₂ from [EMC] and	62

1. INTRODUCTION

Emissions control for the energy sector requires gas sensors that can operate in chemically reactive high temperature environments for both real time monitoring and feedback control of exhaust products. Gaseous species that need to be monitored include hydrogen, hydrocarbons, nitrogen oxides and sulfur oxides. Metal / insulator / semiconductor structures with catalytically active gates are widely used to electronically detect the presence of various chemical species [Spetz 2001]. The wide bandgap semiconductor silicon carbide, SiC, enables device operation to temperatures in excess of 1200 K. In the case of the 6H polytype the energy gap is 3.0 eV, compared to 1.1 eV for silicon. These field-effect devices require a robust dielectric to enable modulation of the semiconductor carrier concentration via an applied gate potential. SiC has a native oxide, SiO₂, which fulfills this need. In addition, SiC is chemically stable in reactive environments making it well suited for sensing applications in harsh environments.

Refractory metal gate SiC devices have been demonstrated for high temperature chemical sensing application by a number of groups [Spetz 2001, Filippov 1999, Hunter 2000, Kim 2001, Nakagomi 2001, Samman 2000, Serina 2001, and Ghosh 2002]. These include hydrogen and hydrocarbon sensors operating at temperatures from 600 K to 1300 K. Specific sensor configurations have achieved millisecond time response and sensitivity at the 0.1% level. The fast response makes the sensors suitable for feedback control. In addition, there are preliminary indications that suitably designed devices may offer sensitivity to ammonia, carbon monoxide, nitrogen oxides and fluorocarbons.

The operation of field-effect devices is dominated by electronic interactions at interfaces. In the case of a metal/insulator/SiC (MISiC) structure, these interfaces are the environment/metal interface, the metal/oxide interface and the oxide/semiconductor interface, which will be studied using a number of spectroscopic techniques. For the SiC sensor technology to fulfill its potential in real world applications the issues of reliability and stability need to be addressed, which requires a detailed experimental study of hydrogen transduction following dehydrogenation at the heated catalytic gate.

A schematic of our catalytic gate SiC field-effect sensor for hydrogen containing species is shown in Figure 1.1. Refractory metal gates such as Pt, Pd and Ir can efficiently dehydrogenate long chain hydrocarbons at temperatures above 700 K. Following dehydrogenation at the heated gate, hydrogen diffuses into the structure.

Fig. 1.1 Schematic of a catalytic gate SiC field-effect sensor for hydrogen containing gases. Typical operation is at $T > 700$ K. Hydrogen can diffuse to both the metal/oxide and oxide/semiconductor interfaces.

For a Si-based catalytic gate sensor operating below 500 K it has been shown that hydrogen gives rise to a polarized layer at the metal/oxide interface [Lundstrom 1976]. This chemically induced polarization charge results in a simple lateral shift of the C-V or current-voltage (I-V) characteristic of the capacitor or Schottky diode sensor, respectively. The magnitude of the voltage shift in these Si based sensors is a measure of the chemically modified metal/semiconductor barrier height.

It has been assumed that the same mechanism describes the operation of higher temperature SiC based sensors for hydrogen containing species. At temperatures above 700 K the diffusion time for hydrogen through 100 nm of Pt and 50 nm of SiO₂ is less than 5 μ s [Katsuta 1979] and 0.5 ms [Beadle 1985] respectively. We have previously demonstrated via *in-situ* C-V spectroscopy of Pt/SiO₂/SiC sensors at 800 K that oxidizing species affect the electronic properties of both the metal/oxide and oxide/semiconductor interfaces [Tobias 2003A]. Fig. 1.2 shows that the C-V characteristic of the sensor in hydrogen is that of an ideal capacitor, within the uncertainty of the experiment. The effect of an oxidizing environment is two fold. First, the C-V characteristic is shifted to more positive potentials, due to chemically induced change in the metal/semiconductor barrier height. Secondly the transition from accumulation to inversion is significantly broadened, indicating the presence of charged states at the oxide/semiconductor interface. Therefore, the mechanisms responsible for hydrogen transduction for Pt/SiO₂/SiC catalytic gate sensors are significantly more complex than that of the lower temperature Si based sensors.

Fig. 1.2 High frequency (1MHz) capacitance – voltage characteristic of a SiC sensor at 800K in 10 H₂ and 1% O₂ (balance gas is N₂). To use the device as sensor, the capacitance is held fixed, while the voltage required to maintain that capacitance is recorded as the sensor signal.[Ghosh 2002].

2. EXECUTIVE SUMMARY

A silicon carbide (SiC) based sensor for the detection of power plant combustion products has been developed. The sensor is a catalytic gate field effect device, Pt/SiO₂/SiC capacitor structure, for detection of hydrogen containing species in chemically reactive, high temperature (600 °C) environments. Device operation in a robust sensor module operating under industrial conditions in the presence of common syngas interferants was demonstrated. The sensor response time is > 1ms to gas exchange. UHV measurements on the Pt gate were used to elucidate the role of oxygen in hydrogen sensing as well as sulfur contamination.

Long term sensor operation in a syngas environment required that we develop a reliable sensor fabrication process to produce operational high temperature SiC sensors. On SiC chip, which contains 52 gates or sensors, we find that up to 70% of the gates have good C-V characteristics at 300 °C. In addition we routinely perform sensor measurements on our largest devices (diameter of 1mm) at 620 °C. A large area device is attractive for sensing applications as the device capacitance scales with area, and the signal to noise ratio is proportional to the slope of the C-V characteristic. Two of the sensor chips remain operational after ~75 hours of testing at 600 °C, which consists of $\geq$ 13 cycles between room temperature and 600 °C. These samples were oxidized by Prof. John Williams at Auburn University. In addition the robustness of the Pt sensing films has up to 800 °C has been demonstrated.

High-temperature reliability is crucial for practical sensor applications. A primary failure mode of SiC devices for power applications is oxide breakdown caused by electron injection from the substrate. Monitoring the gate leakage current as a function of time, temperature and electric field is a standard technique used to determine mean-time-to -failure of metal-oxide-semiconductor (MOS) structures. We have investigated the high-temperature reliability of *n*-type SiC MOS sensors by monitoring the gate leakage current as a function of temperature. We have measured devices made on both the 4H and 6H polytypes of SiC at temperatures up to 600 K and electric field strengths up to 0.6 MV/cm. This electric field is small compared to those usually encountered in power applications, but is appropriate for our sensors, since we have determined that the optimum bias for gas sensing is near midgap. We find leakage current densities below 17 nA/cm² at 600 K and below 3 nA/cm² at 450 K. These are promising results for high temperature operation.

We have built and tested a time-resolved fast sensor test set-up for gas sensors. We can record the fast components of the sensor response with millisecond resolution while at the same time, also capturing the slower components of the response, such as the steady state value. Using Laser Induced Fluorescence (LIF) imaging, we have quantitatively determined that for a 1mm diameter sensor the gas is completely exchanged in 1.2ms. The sensor is characterized under standard industrial sensor operating conditions, including gas pressure and device temperature (300 – 650 °C), while using flows typically found in a research laboratory. As such, our set-up is unique in that we do not have to resort to extremely high gas flows [Gerblinger 1991] or vacuum techniques [Kelleter 1992] for rapid transport of gas analytes to the sensor surface. An industrial colleague has expressed his interest in replicating our test set-up for qualifying commercial planar gas sensors. We have used the system to characterize a Pt/SiO₂/SiC

sensor at 650°C and found response times of less than 0.6 ms to a gas exchange from oxygen to hydrogen.

Ultrahigh Vacuum Chemistry

Ultrahigh vacuum (UHV) surface chemistry experiments can be an invaluable complement to standard experiments carried out near atmospheric pressure. Although the gas pressures and flow rates differ by orders of magnitude between the two types of study, decades of experience in catalytic surface chemistry have shown that UHV experiments can probe the same fundamental reaction and transduction mechanisms, under similar conditions of surface and interface coverage and similar ratios of the relevant reactant gases. Further, the control of gas exposure and surface sensitive spectroscopies available in the UHV environment allow detailed mechanistic investigations that are not possible at higher pressures. In the case of the silicon-based MOS gas sensors that are the prototype for the MISiC sensors studied here, UHV experiments provided valuable insights into the fundamental processes of sensor operation [Petersson 1985, Eriksson 1997]. To our knowledge, there have been no prior UHV studies of MISiC sensors.

Using the equipment and techniques described above, we have carried out initial studies of hydrogen sensing behavior in the UHV environment. We have measured C-V curves of several devices at various temperatures (up to 800 °K) and while exposing the devices to hydrogen and oxygen at partial pressures from 10^{-8} to 10^{-5} Torr. We have monitored sensor response while varying the gas environment, and have observed consistent and repeatable response to hydrogen and oxygen at fixed temperature, with a sensitivity of 7 mV/decade at 600 °K.

The results provide important input to our developing model of hydrogen transduction mechanisms. Our experiments demonstrate that, in the absence of oxygen, hydrogen transduction at 600 °K is only partially reversible, while the presence of oxygen makes it fully reversible. This observation suggests the existence of at least two types of interface sites for hydrogen. Our results also suggest that the process of catalytic gate “activation,” which is critical to device function but remains incompletely understood, has at least two aspects. One is cleaning of the Pt gate surface, which occurs under UHV conditions but, by itself, gives rise to hydrogen sensitivity less than one-tenth that achieved on devices activated at atmospheric pressure. The additional sensitivity appears to arise from the creation of a higher surface density of active transduction sites due to roughening of the gate.

Initial experiments on sulfur contamination in UHV have shown that it is possible to develop high surface coverages of sulfur when the gate is exposed to hydrogen sulfide at elevated temperatures, even in the presence of oxygen or hydrogen. Once deposited, the sulfur is difficult to remove chemically, even at low sulfur coverages. Under vacuum conditions we have been able to remove it only by ion sputtering. To date these experiments have been carried out only on non-functional devices, so we cannot yet draw a direct connection between sensor response and sulfur contamination.

During the second phase of the project UHV studies focused on the response of the device to gases other than hydrogen. We carried out experiments on hydrocarbon sensing, using the unsaturated linear hydrocarbon propene (C_3H_6) as a prototypical model analyte. The device showed a strong response to propene, significantly stronger than to

hydrogen. The enhanced sensitivity may be simply due to the larger number of hydrogen atoms per molecule in the hydrocarbon. As with hydrogen, sensing experiments in a constant oxygen background show a transition between hydrogen-deficient and oxygen-deficient regimes, with anomalously high sensor response (~ 750 mV/decade for propene) in the transition region. This similarity suggests that the mechanism of propene sensing is the same as for hydrogen sensing, involving the bonding of hydrogen atoms released by surface decomposition to sites at the metal/oxide interface where they can induce a bias shift. Auger measurements indicated that propene exposure leaves carbon behind on the gate surface, which can be at least partially removed by exposure to oxygen.

An experiment to investigate sensor response to carbon monoxide was also attempted, but the results were inconclusive. Poor signal-to-noise ratio, combined with a hydrogen background that varied with the CO level, prevented any definitive conclusions regarding the response to CO.

The role of oxygen in the functioning of silicon carbide field-effect gas sensors with non-porous platinum gates was also investigated with UHV techniques. The devices studied are shown to be sensitive both to hydrogen and to propene. All of the results are consistent with oxygen acting through its surface reactions with hydrogen. Three specific aspects are highlighted: the need, under some conditions, for oxygen to reset the device to a fully hydrogen-depleted state; competition between hydrogen oxidation and hydrogen diffusion to metal/oxide interface sites, leading to step-like behavior as a function of the oxygen/hydrogen ratio (λ -sensing); and the removal of sulfur contamination by oxygen.

The subcontract with Tufts University concluded on February 28, 2007. The Tufts part of the project, encompassing ultrahigh vacuum studies of the sensor surface chemistry, terminated as of that date.

Industrial Testing

In collaboration with Dr. Benjamin Chorpene from NETL we have demonstrated the viability of using our SiC device as a hydrogen sensor for monitoring the combustion of low sulfur fuels or in a fuel reformer application. Two separate week long tests of our gas sensors in the reactors at the NETL facility in Morgantown, WV (during June 2005 and October/November 2006) were successfully completed. All components of the sensor module, mechanical, electrical and data acquisition software performed as designed for the entire period. The only exception was degradation of the Au wire bonds following exposure to a 350 gas stream containing water vapor and H₂S. Note that neither the sensor nor the module were damaged. The module was designed for ease of use by a qualified technician. For both tests two modules were shipped to NETL and installed by the reactor technicians. All the devices on the two sensor chips in both modules were characterized at MSU and found to be functional hydrogen sensors at 600C. The sensor sensitivity is logarithmic over 3.5 decades of hydrogen concentration.

For the first industrial test, all the data for the week long run at NETL was collected from a single large area sensor. . At NETL the logarithmic behavior of the sensor response was confirmed up to higher hydrogen concentrations (50%) and the SiC sensor results were validated with an in-line mass spectrometer. Standard interferants such as CO, CO₂ and CH₄ had a small effect on the sensor, and the device continued to

function normally after exposure to H_2 . The temperature range of the experiments was limited to 370 °C by the capabilities of the micro-reactor.

In consultation with Susan Maley we identified typical stream compositions and conditions for potential applications for our SiC based hydrogen gas sensor. These include monitoring the gas stream in a syngas application and in the “Cold gas cleaning process” of integrated gasification combined cycle (IGCC) gasifiers.

During the second test at NETL (Oct/Nov 2006) we demonstrated that the device can be used as a hydrogen monitor in syngas applications based on typical compositions reported by Tampa Electric Company’s Polk Power Station. Sensing measurements were performed in the Catalyst Screening Unit (CSU) located in Building B3 (area 150) at the NETL facility in Morgantown, West. Dr. Stephen Beers (NETL) provided us support on the mass spectrometer measurements and Mr. Thomas Simonyi (NETL) provided the gas chromatography analysis of period gas “grabs” taken while running the reactor. The goal of these experiments was to make measurements in hot (350 -550 °C) hydrogen gas streams (~1000 sccm), containing the interferents CO , CO_2 , CH_4 as well as H_2S and water vapor.

As in the first test all the measurements are from a single 1 mm gate on the chip, which demonstrates the robustness of our sensor fabrication techniques. The sensor response to hydrogen gas at 350 °C is 240 mV/decade, this is significantly higher than the device response to room temperature gas or that predicted from vacuum chamber studies. A downstream mass spectrometer validated the SiC sensor results. The sensor can monitor the net hydrogen concentration in the presence of the following common interferants: CO_2 (10 – 18 %), CH_4 (1 %) and CO (31 – 52 %). The sensor performance was not degraded by 8 hours of cumulative exposure to ~1000 ppm of H_2S . Neither did 10 hours of exposure to 5 – 15 % water vapor, followed by 5 hours of 15 % water vapor with 1000 ppm of H_2S poison the device.

Our original plan was to (i) first determine the SiC sensor response to pure 1-60% hydrogen without any interferants, (ii) second to systematically vary the CO (38 – 45%) and CO_2 (9 – 16%) level, keeping methane fixed at 1%, test these conditions for 28, 40 and 48 % H_2 (iii) third to repeat the experiments in (ii) with 200 ppm of H_2S , note that this is the typical level for commercially clean syngas, (iv) and finally fourth to repeat (iii) with 15% water vapor. We were able to show that the CSU could deliver up to a 550 °C gas stream to the sensor module, so our plan was to make sensing measurements at 350, 450 and 550 °C to cover some of the expected temperature range of syngas.

However, we had to spend a considerable amount of time “shaking down” the CSU reactor setup and introduction of *known* amounts of sulfur and water was not possible. Due to our limited experimental time at the CSU, we reformulated our plans on-site abandoning the systematic approach and concentrated on the following “key” conditions. (i) The SiC sensor response to 1-60 % hydrogen without any interferants was measured at only 350 °C. All subsequent measurements were made with a 350 °C gas stream. (ii) In the absence of sulfur we showed that for a 37 % H_2 gas stream CO (41-46%) and CO_2 (10-14%) level, keeping methane fixed at 1% did not affect the performance of the hydrogen sensor. (iii) Repeating test (ii) in the presence of 50-100 ppm sulfur modified the sensor signal by only a few percent. In addition following 8 cumulative hours of ~740 ppm of H_2S , the hydrogen response of the sensor from 1-60 % H_2 changed by only 6%. (iv) The sensor was not adversely affected by 5-15 % water vapor.

Detailed thermometry measurements of the temperature of the Pt catalytic gate were performed in the catalyst screening unit with hydrogen gas from 300 to 500 °C. We found that the temperature of the Pt gate was consistently (49 ± 1) °C lower than the backside heater. An automated system for controlling the sensor temperature is under construction. From these experiments we also postulate that the catalytic processes at the Pt sensing film responsible for hydrogen transduction are a dynamic process dependent on the kinetic energy of the gas though the gas temperature and flow rate.

Following 8 days of measurements in the harsh industrial environment of a syngas stream which included sulfur and water vapor, the sample had erratic electrical characteristics. Examination of the chip upon return to MSU showed that the sensing chip was covered with a large amount of debris that caused electrical shorts and failure of the Au wire bonds. Upon repairing the electrical connections the sensor response to 50ppm – 60% hydrogen *increased* by a factor of 6, demonstrating that in no way was the Pt/SiO₂/SiC device poisoned by the industrial measurements.

Catalytic Activity Platinum Sensing Film

The sensor response to hydrogen gas at 350 °C is 240 mV/decade, this is significantly higher than the device response to room temperature gas or that predicted from vacuum chamber studies [Dannetun]. The enhanced catalytic activity of the platinum sensing film under energy plant operating conditions was investigated using (i) optical microscopy, (ii) atomic force microscopy, (iii) x-ray diffraction, (iv) transmission electron microscopy and (v) x-ray photoelectron spectroscopy. Samples exposed to several distinct conditions were characterized, (a) “as deposited” Pt films, (b) Pt films which have been “just activated” by exposure to alternating pulses of room temperature hydrogen and oxygen, (c) post “long term industrial reactor” testing performed at the DOE Morgantown facility and (d) post “long term laboratory” testing for several months at MSU. Note that the SiC substrate temperature is 600C during all gas measurement, irrespective of the gas temperature itself.

Optical microscopy indicates that the surface of “As grown sample” and “Just activated sample” remain smooth. On the other hand those devices which have been exposed and operated in high temperature gas, or has been operated in room gas for a long period of time developed rough surfaces.

From AFM images we find that: the “as grown” sample has relatively smooth surface morphology with 0.5-2 nm RMS roughness and there is evidence of different size of grains on the surface. On those samples which have been “just activated” we observe creation of some holes in the Pt films. We postulate that these are happening at the grain boundaries and are caused by grains that find it energetically favorable to emerge into each other to reduce the grain boundary stress. These movements of grain boundary and formation of larger grain increases as the temperature of exposed gas increases “post industrial reactor” or if the device operate at room temperature gas “post lab reactor”.

We have compared the XRD data of all samples, and from a structural point of view, the Pt gates on all devices, regardless of the history of the devices and what they have been through, the Pt layer is face-centered-cubic, fcc, (111). This is the lowest energy phase for epitaxial Pt. The as grown sample which is a polycrystalline film has

some strain in it. Following exposure to high temperature gas much of the strain is released giving a Pt and has a peak value close to expected 39.73° .

The XPS measurements showed that there is some residual carbon (adventitious) on all the surface of all the sensing films. During sputter depth profiling the Pt 4f, the O 1s, the Si 2p and C 1s peaks were monitored. Both the as deposited and activated samples show a well defined Pt, SiO₂ and SiC layers, with some hint of an oxycarbide region. However after the industrial and laboratory testing the Pt signal at the surface is reduced, by a factor of at least two and extends significantly deeper into the sample. In addition oxygen and silicon are observed through out most of the sample. Carbon is observed after about 80s of sputtering.

Transmission electron microscopy (TEM) samples were prepared, and high resolution TEM images were obtained along with electron dispersion spectroscopy (EDS). The TEM of the as-deposited sample revealed a well-defined single crystal SiC substrate, a continuous amorphous layer of SiO₂, and a continuous columnar polycrystalline layer the Pt (sensing gates). In sample with activation only, subtle morphological changes were observed in the layer structure with presence of some pinholes. In the sample which went through the operation in Industrial Reactor environment (NETL - Morgantown), significant morphological changes were noted in the devices. Most striking was the change in the appearance of the Pt to a much more rounded islanded morphology, with significant pin-holes.

We find that exposure to high temperature gases significantly modifies the morphology of the Pt catalytic film and the Pt/SiO₂ interfacial region, which we tentatively attribute to the enhanced hydrogen sensitivity of the sensing film.

During 2006 Ruby Ghosh engaged in a number of discussions with Dr. Michael Swanson at the Energy & Environmental Research Center (EERC), University of North Dakota and Dr. Michael Ursey at Sporian Microsystems Inc. regarding a "coupon" test of our SiC sensor in an IGCC gasifier. During this reporting period, EERC did not receive the external funds necessary to operate the facility, preventing coupon testing of our sensor.

R. Ghosh presented a summary of the project results to Susan Maley and Robert Romanosky at the NETL lab in Morgantown, WV on Nov. 19, 2007.

From a project management perspective, Dr. Yung Ho Kahng joined the project as a postdoctoral associate in July 2004, working on the UHV experiments; in Oct 2006 2006 he assumed a postdoctoral position at the Korean Research Institute of Standards and Science (KRISS). A graduate student, Mr. Wei Lu, worked on the UHV experiments from September 2006 to February 2007. Dr. Peter Tobias was the postdoctoral researcher at MSU from October 2003 through mid April 2005. Upon completion of his postdoctoral position he obtained a permanent staff position in the Microdevices Advanced Technology group at Honeywell Laboratories in Minneapolis, MN. Dr. Reza Loloee, a Research Specialist with the Dept. of Physics at Michigan State University, joined the effort in March 2005, assuming the responsibilities previously performed by Peter Tobias through September 2008.

The subcontract with Tufts University concluded on February 28, 2007. The Tufts part of the project, encompassing ultrahigh vacuum studies of the sensor surface chemistry, terminated as of that date.

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Conference Presentations and Seminars

P. Tobias, "Sensing mechanisms of high temperature silicon carbide field-effect devices" TRANSDUCERS 2003, 12th International Conference Solid-State Sensors, Actuators and Microsystems, June 9-12, 2003, poster presentation.

R. Ghosh "High temperature SiC chemical sensors: an in-situ study of gas response mechanisms" at the 2003 International Symposium on SiC and Related Materials, Oct 5 - Oct 10, 2003, Lyon, France

P. Tobias, "Sensing mechanisms of SiC devices for exhaust gas applications", 2nd IEEE Int. Conf. on Sensors, Oct. 21 -24, 2003 in an invited session on "Extreme Environmental Chemical Sensors", Toronto, Canada.

R. Ghosh was invited to present the solid state physics seminar at Michigan State University on Nov. 17, 2003.

R. Ghosh was invited to present the physics colloquium at Auburn University on Jan. 23, 2004.

R. Ghosh presented the Semiconductor Electronics Division Seminar, at the National Institute of Standards and Technology, Gaithersburg, MD on June 2, 2004

R. Ghosh "High Temperature Operation of SiC Electronics and Sensors" at the 2004 Electronic Materials Conference, June 23 -25, 2004, University of Notre Dame, South Bend IN.

P. Tobias and R. Ghosh, "Millisecond response time measurements of high temperature gas sensors", 3rd IEEE Int. Conf. on Sensors, Oct. 24-27, 2004, Vienna, Austria.

R. Ghosh was invited to present the physics seminar at Calvin College, Grand Rapids, MI on Feb. 8, 2005

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3. EXPERIMENTAL

3.1 Sensor fabrication, activation and characterization

The n-MOS capacitors were fabricated on 6H-SiC (N type) substrates (3 μm , $2.1 \times 10^{16} \text{ N/cm}^3$ epitaxial layer). The gate oxide ($\sim 39 \text{ nm}$) was grown via dry oxidation at 1150°C , followed by a 900°C Ar anneal and a 2 hour 1175°C NO anneal. The gate oxidation was performed by Prof. John Williams, Dept. of Physics, Auburn University. The gate metal is 100 nm of Pt sputtered at 350°C in a 2.5 mTorr Ar atmosphere. Each SiC chip consists of an array of 52 gates with nominal diameters of 200 to $1000 \mu\text{m}$. The high frequency (1 MHz or 100 KHz) C-V characteristics were measured using the Interactive Characterization Software (Metrics) and a Keithley 590 high frequency capacitance meter. The noise in our electrical characterization system is $\pm 2\text{pA}$ for the current-voltage (I-V) measurements and is $\pm 2\text{pF}$ for capacitance-voltage (C-V) measurements, all at 630°C .

The activation of these SiC gas sensors takes place by switching between oxidizing and reducing gases, to obtain a fast and stable sensor response. All the devices on the SiC sensor chips were activated in an "activation chamber" simultaneously by flooding the entire chip with gas at about 600°C . In the activation process, alternately, 1.0% O_2 and 10% H_2 are sprayed onto the entire face of the SiC chip, which is heated by the micro heaters. The signal from one of the sensors is monitored during the activation process. The sensor measurements were made by monitoring the gate voltage, while holding the capacitance fixed at near midgap bias.

Fig. 3.1.1 Photograph of the inside of the test module showing SiC sensor chip (1 cm^2).

For sensor measurements at real application sites, we have developed with Mr. Nate Verhanovitz (Troy Inc.) a program for sensor control and data acquisition. The required hardware is a PC with operation systems Windows XP or 2000 and with a GPIB-card, e.g. from National Instruments, a GPIB cable and the 7200 capacitance meter from Boonton.. For flexibility in harsh measurement environments, a laptop can be used as the measurement computer. The program is intended for sensor response measurements in the 0.5 s regime. As in the case of the C-V characterization program this program runs as a self-contained executable, requiring only a PC or laptop with a GPIB data acquisition card.

3.2 *Photoemission measurement technique*

We have built a module for performing photoemission spectroscopy on our SiC samples; see Fig. 3.2.1 for a schematic. The module was developed to be used inside a commercial spectrometer (Fluorolog-3, Instruments SA). The Fluorolog-3 instrument contains the UV light source (150W ozone generated Xe lamp); a single-grating monochromator to set the bandwidth and center wavelength of the beam incident on the sample; a single grating exit monochromator and photomultiplier tube (multi-alkali PMT tube, Hamamatsu R928) to detect the generated photoelectrons and a digital/analog card that allows us to record the PMT signal as a function of incident photon wavelength or time. A Si photo-diode in the Fluorolog instrument was used to monitor the incident photon energy. The sample cell itself was designed to allow optical access to the sample for the incident pump beam, locally heat the SiC sample between 23 and 600 °C and control of the gas environment inside the cell (to alternate between oxidizing and reducing environments).

Fig. 3.2.1 Schematic of the set-up for photoemission measurements with a heated SiC sample in a UV transparent gas-flow through cell.

3.3 Sensor measurements in an “industrial” reactors at NETL, Morgantown, WV

2005 Measurements – B3 microreactor, NETL

Two complete test modules with their sensor chips were shipped to Morgantown, WV via a commercial carrier and one was installed in the micro-reactor in the B-3 area (see Fig. 3.3.1) by the reactor operators at NETL. The photograph below shows Test module #1 with its electrical breakout box, connected to the micro-reactor. The input to the micro-reactor consists of an array of gas flow lines with electronically controlled pneumatic valves and mass flow controllers, which are controlled by the Procedia software. A 700 °C furnace heats the incoming gases and the furnace itself is housed inside a conditioning box maintained at 200 °C. The gas leaving the conditioning box through a ¼” stainless steel tube (labeled “input gas” in the photo) was connected to the union cross of the test assembly. As the SiC sensor was located about 30 cm from the conditioner, heater tape (Omega - STH051) and insulation was wrapped around the ¼” tubing coming into the sensor (labeled input gas), the union cross and the gas line returning to the conditioner (labeled output gas) to maintain gas temperature. The gas temperature inside the union cross, approximately one centimeter away from the SiC sensor was monitored with a thermocouple. Our measurements during the week long run were limited to a gas temperature of 350 – 370 °C in this setup. Note that the SiC sensor itself was heated to 600 °C during all the measurements to maximize the magnitude and response time of the sensor signal.

Fig. 3.3.1 Photograph of SiC sensor test module installed in the micro-reactor facility in building B3 during the week long test run (June 13 – 17, 2005) at Morgantown, WV. The computer for automated sensor data collection is outside the field of view.

An in-line mass spectrometer located about 13 m downstream from the SiC sensor was used to validate the sensor data. The difference in location between the SiC sensor and the mass spec resulted in a few seconds of lag time between the responses of two instruments. Time synchronized data from the Procedia software (controller for all gas lines, mass flow controllers and the thermocouple output), mass spectrometer and SiC sensor were collected. These will be used to estimate the approximate lag time between SiC sensor and mass spec.

Fig. 3.3.2 shows the sensor test “team” Dr. Benjamin Chorpening (NETL), Dr. Ruby Ghosh (MSU) and Dr. Reza Loloee (MSU).

Fig. 3.3.2 SiC sensor test “team”: from NETL - Dr. Benjamin Chorpening (standing), and from MSU- Dr. Ruby Ghosh (standing) and Dr. Reza Loloee (seated)

2007 Measurements - Catalyst screening unit (CSU) NETL

In order to ascertain the performance of the SiC sensor under model syngas conditions, sensing measurements were taken in the Catalyst Screening Unit (CSU) located in Building B3 (area 150) at the NETL facility in Morgantown, West Virginia between October 30 and Nov 8, 2006. The goal of these experiments was to make measurements in hot (350 -550 °C) hydrogen gas streams (~1000 sccm), containing the interferernts CO, CO₂, CH₄ as well as H₂S and water vapor. Fig. 3.3.3. (top left) shows the test module mounted between two powerful clam-shell heaters, the upper heater is open and the lower heater is closed. The purpose of this configuration was to ensure a uniform and stable temperature through out the entire sensing module. A K-type thermocouple located inside the union-tee holding the module was use to monitor the gas temperature. We were able to achieve gas temperatures of 350 – 520 °C in this setup, which is considerably higher than the 350 C we obtained from measurements in the High Performance Reactor in June 2005. In the center of union-tee we mounted a diverter to direct the gas flow directly onto the face of SiC sensor.

The CSU was supplied reactant gases through an array of gas flow lines with electronically controlled pneumatic valves and mass flow controllers, supervised by industrial control software. An in-line mass spectrometer located about 10 m downstream from the SiC sensor was used to validate the sensor data. This validation process worked well in real-time for H_2 , CO , CO_2 , CH_4 , N_2 , and O_2 . However due to calibration issues the real-time, on-site measurements of H_2S were not always reliable, the data we report has been post-processed following the 8 day data collection period. During the experiments we determined the actual H_2S level at the sensor model via gas chromatography analysis of “gas grabs” taken from the inlet and outlet of the reactor. The gas chromatography results were typically available to us within 1-2 hours. Note that the difference in location between the SiC sensor and the mass spec resulted in ~2 min of lag time between the responses of the two instruments. Time synchronized data from the industrial control software (controller for all gas lines, mass flow controllers and the thermocouple output); mass spectrometer and SiC sensor data acquisition software were collected. The data presented here has been corrected for the time lag between the various instruments.

Calibration of mass spectrometer

The mass spectrometer was manually calibrated by Dr. Stephen Beer with gas mixtures of known compositions. He then post-processed the data to check to see if there were problems with the mass spectrometer calculation routine during the actual run. His post processed calculation is in reasonable agreement with the mass spec numbers displayed in real time. This was done in case the mass spec gives bogus numbers due to the embedded computer and the host PC becoming desynchronized.

The H_2S calibration was done by first running with air to determine the mass 34/32 ratio for oxygen so one can subtract the O_2 contribution from the total mass 34 signal. The rest of the signal at 34 comes from the H_2S molecular ion and fragments of SO_2 . The fragmentation pattern of SO_2 from the SO_2 calibration gas was measured and subtracted out, the remainder of the mass 34 was assigned to H_2S . Typically, the H_2S sensitivity factor was obtained from a 3.00% H_2S calibration gas standard

Fig. 3.3.3 Photograph of the setup for both thermometry and sensor measurements in the Catalyst Screening Unit at NETL- Morgantown West Virginia

3.4 *Pt film characterization*

Optical Microscopy

First step for characterizing the gate surface morphology due to activation processes or long time operation at high temperature was collection of both Bright-field (BF) and Dark-field (DF) images of a few selected devices at different stage of experiment. The Nikon eclips LV100 was used for collecting these images. This optical microscope has 1.25X, 5X, 20X, 50X and 100x Lu Plan Flour objectives.

Atomic Force Microscopy

Atomic force microscopy (AFM) was used as a complementary technique to study the topography of the Pt gates before and after activation as well as after long term sensing operation. The digital instrument (DI) Dimension 3100 was used for this purpose. This system, which is a very versatile, scanning probe microscope, supports all popular scanning modes such as atomic force microscopy (AFM).

X-ray Photoemission Spectroscopy

Micro-spot X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD instrument. The x-ray source is an Al monochromatic source with a pass energy of 40 eV and the analyzer is located normal to the sample surface. Using the imaging mode of the instrument the 110 μm spot was positioned well inside a 1000 μm diameter Pt gate. Initially broad spectra from 0 to 1100 eV were collected to identify the elemental species on the surface. Then energy resolved spectra were obtained of the (i) Pt 4f line (68 to 84 eV), (ii) Si 2p line (94 to 110 eV), (iii) C 1s line (275 to 300 eV) and (iv) O 1s line (525 to 545 eV).

Depth profiles of the elements was performed by sputtering using a 3.8 KeV, 3 x 3 mm rastered Ar^+ beam. The sample was etched for 10 min, the Si, O, C and Pt spectra were collected at 15 time intervals. The spectra for each element were averaged at least four times.

X-ray Diffraction Measurements

The structure of the Pt gates was investigated by collecting x-ray diffraction (XRD) patterns from several samples, before and after activation process and after operation in harsh industrial environment. A Rigagu Rotating anode powder diffractometer was used to collect the diffraction data form several samples.

Transmission Electron Microscopy

Cross-sectional samples for TEM examination were produced from specific devices of interest using an FEI Nova Dual Beam Focused Ion Beam. Prior to this sample preparation, the samples were sputter coated with a 1 μm thick layer of Nb. This allowed for further Pt protective cap coating, typically carried out using reactive gas/ion

beam interaction and used to protect the regions of interest from excessive ion beam damage during sample preparation, to be distinguished from the Pt layer of interest in the devices. Sample lift out was performed in-situ using a Kleindiek Nanotechnik nanomanipulator. Ion milling was performed using 30 kV Ga ions with decreasing beam currents with smaller probe sizes as the samples thinned, with the final thinning carried out using a beam current of 0.1 nA.

During the sample preparation, FEG-SEM images of the sample and cross-sections collected to provide additional insight in to the morphology of the device layers TEM was carried out on a JEOL 2010F and a JEOL 3011 operated at 200 kV and 300 kV respectively, with EDS performed at 200 kV using an EDAX r-TEM Ultra-thin window Si-Li x-ray detector.

3.5 *Ultrahigh vacuum measurements*

Reproducible surface chemistry measurements require the ability to prepare an atomically clean surface *in situ*. Surface cleanliness is generally determined with Auger electron spectroscopy (AES), which measures the energies of secondary electrons emitted from the surface when it is bombarded with high energy (2 keV) electrons. The energies are characteristic of the specific elements present on or near the surface. The primary contaminants on the Pt surface are carbon, sulfur and oxygen. The upper curve in Fig. 3.5.2 shows an AES spectrum of a sample contaminated with sulfur and carbon. The contaminants are removed primarily by sputtering in 5×10^{-5} Torr Ar at 850 K for 40 minutes followed by annealing to 1000 K to restore surface order. Sputtering always leaves a small amount of carbon on the surface, however, due to unavoidable CO in the sputtering gas. This residual carbon is removed by heating the sample at 800 °K in 1.5×10^{-7} Torr oxygen for 30 minutes. The Auger spectrum of the sample after cleaning; no peaks other than those attributable to Pt are detectable. (Note that the peak near 150 eV includes contributions from both Pt and S; the intensity of that peak relative to the other Pt peaks in the lower spectrum is characteristic of clean Pt.)

Temperature programmed desorption

Temperature-programmed desorption (TPD) is a standard technique in surface chemistry for measuring adsorbate surface coverages, binding energies, and for identifying and characterizing surface chemical reactions. The sample is exposed to one or more gases at a sufficiently low temperature (typically ~100 K) that the gases stick to the surface and do not react. The sample is then heated at a linear rate, $dT/dt \sim 5$ K/s, and the gases evolved from the surface are detected with a quadrupole mass spectrometer (QMS).

Fig. 3.5.1. Schematic diagram of the electrostatic shield and negatively biased repeller grid used to prevent stray electrons from the heating filament from entering the QMS head and interfering with TPD measurements.

Fig. 3.5.1 shows a schematic diagram of the system. The QMS head is surrounded by an electrically grounded shield with an aperture facing the sample for the entry of molecules desorbing from the surface. In front of the aperture is an electrically isolated wire grid, which is biased at a high negative potential (typically ~ -1200 V) to repel any negatively charged ions or stray electrons emitted by the heater filament.

Fig. 3.5.2 compares simulated TPD scans measured with no bias applied to the grid and with a bias of -1200 V. In these measurements the masses observed correspond to nonexistent species, so the real signal should be zero. The large spurious signals during heating seen without bias are largely eliminated when the grid is biased at -1200 V.

Fig. 3.5.2. Pressure-time traces measured by the QMS during sample heating, for two masses (5 and 37 amu) at which no real signal is expected. For the upper pair of graphs no bias was applied to the grid, and a strong spurious signal is observed in both mass channels during heating. In the lower traces, a bias of -1200 V was applied, and the spurious signal is dramatically reduced.

Techniques for studying sulfur contamination

Sulfur is frequently present in significant concentrations, usually as H_2S , in practical sensing environments, including those relevant to coal combustion and gasification. Adsorbed sulfur is well known as a “poison” for its ability to eliminate the catalytic activity of transition metals, such as platinum. On the other hand, catalytic oxidation and reduction of adsorbed sulfur can also take place under some conditions, providing self-cleaning of the surface. To investigate the possible effects of sulfur on our sensors, we are developing procedures to study sulfur contamination and removal.

We have shown that sulfur can be reproducibly deposited on the Pt surface in controlled amounts by exposing the sample to H_2S at room temperature. The amount of adsorbed sulfur can be measured with Auger spectroscopy.. Adsorbed sulfur can be removed by argon ion sputtering. Reactions of adsorbed sulfur with other gases can be studied either by heating the sample in the desired gas, followed by Auger spectroscopy, or by TPD, with the two gases coadsorbed at low temperature. In the latter case a reaction is demonstrated by the desorption of the reaction product (e.g. SO or SO_2 from coadsorbed sulfur and oxygen) as well as by changes in the sulfur Auger signal.

Fig. 3.5.3 UHV sample mount. The ring with keyhole slots is the sample carrier, which can be loaded in and out of UHV without breaking vacuum. A 1 cm² prototype Pt/SiC sample is shown clipped to the center of the ring. The mounting system permits sample heating and cooling (120 to >1200 K), and multiple electrical contacts.

UHV sample mount design

Alumina substrates with thick-film gold pads were used for mounting and making electrical contact to SiC samples. The assembly was baked in air on a hot plate at 200 - 300°C before being loaded into the UHV chamber. We have determined that this mounting system withstands multiple (>20) heating and cooling cycles between 200 K and 1000 K without failure; does not outgas appreciably during heating, and provides excellent thermal contact between the header and the sample.

Silver paste was also used to bond a fine-wire Type K thermocouple to the front of the sample for temperature measurements. (In UHV measurements, where the ambient gas density is so low that its thermal conductivity is negligible, the sample is far from thermal equilibrium with its environment, so it is essential that the thermometer be mounted either directly to the surface of the sample or very close to the sample on the alumina header.) This bond has also remained intact through multiple heating/cooling cycles, and comparison of carbon monoxide temperature-programmed desorption measurements with published data indicates that the measured temperature deviates from the actual surface temperature by less than 50 K.

Gas pressure calibration

Measurements of gas partial pressure in UHV are based on ion current measurements from a quadrupole residual gas analyzer (RGA) (Balzers Prisma 200). Because of differences in molecular mass and ionization efficiency, the sensitivity of the RGA can be different for different gases. To obtain more accurate measurements of gas partial pressure, we calibrated the RGA signals against the ion gauge total pressure reading. Ion gauge pressure readings were corrected for different gas species' sensitivity [Summers 1969]. The ratio of true pressure to RGA signal was 0.4 for hydrogen and 1 for oxygen. Fig. 3.5.4 shows the calibration results for hydrogen and oxygen. This method could not be used for hydrogen sulfide, because the pressure of other gases was always greater than that of the H_2S , due to chemical interactions in the vacuum pumps and on the chamber walls. All that could be determined was that for H_2S the RGA reading and actual partial pressure are consistent within an order of magnitude.

Fig. 3.5.4. Calibration of RGA signal against actual pressure for hydrogen and oxygen.

Software development

As another step in the development of an integrated suite of software applications for the UHV experiments, we have developed a Labview-based PID temperature control system. The system includes a commercial USB digital/analog converter (National Instruments USB 6009), with home-built DC amplifiers to match the analog output of the converter to the required control inputs of our filament and high voltage power supplies. We have written two temperature control programs in LabView, one for constant temperature operation, and one for generating linear temperature ramps for temperature-programmed desorption. In both programs the filament power is kept fixed, and the high voltage of the electron bombardment system is controlled by feedback to maintain either a constant temperature, or a constant rate of change of the temperature. Figs. 3.5.5 show the Labview front panels for one of these programs.

Fig. 3.5.5. Front panel of the constant-temperature PID control program. The upper graph shows the temperature, while the lower graph shows the high voltage. The fluctuations in the high voltage occur when different gases are admitted to the chamber, but the temperature remains stable until the regulation is terminated.

4. RESULTS AND DISCUSSION

4.1 *High Temperature Oxide Reliability*

Optimum sensor operating point

SiC MOS device operation in chemically corrosive, high temperature environments places stringent demands on the stability of the insulating dielectric and the constituent interfaces within the structure. The primary mode of oxide breakdown at elevated temperatures is attributed to electron injection from the substrate [Maranowski 1998, Dimitrijevic 2003]. To minimize the deleterious effects of oxide breakdown it would be advantageous to operate the MOS device in a regime where the electric field across the oxide is minimized. For our n-type SiC MOS structures biased at midgap, we measure electric field strengths below 0.6 MV/cm at temperatures up to 300 K. Therefore we postulate that the optimum sensor operating point with respect to long term device reliability at high temperatures is at midgap.

Gate leakage current measurements at high temperature

The gate leakage current as a function of gate voltage and temperature was measured from room temperature to 600 K in laboratory air. Only the higher temperature results above 450 K are shown in Fig 4.1.. The current density was evaluated at the midgap gate bias. The current densities are for four different gates fabricated on two separate 6H-SiC samples. The error bars in both figures do not reflect the device quality, rather they are due to the ± 2 pA measurement uncertainty on the hot chuck. Below 500 °K the leakage current is approximately constant and begins to increase between 550 and 600 K. Note that the electric field across the oxide at midgap for all the devices is low, < 0.6 MV/cm up to 600 K. Within our small measurement set, no correlations between gate diameter, metallization technique or gate material, oxidation method or oxide thickness were observed.

Our results are very encouraging in terms of the reliability of SiC MOS devices at elevated temperatures. For oxide fields below 0.6 MV/cm we obtain current densities < 10 nA/cm² and < 17 nA/cm² at 600 K for the 6H and 4H polytypes respectively. The results are independent of gate diameter, which ranged from 220 - 550 μ m. Biasing at midgap significantly reduces the field across the gate oxide, which in turn lowers the oxide current, resulting in longer device lifetimes at higher temperature. Note that at high temperature our 4H-SiC results are similar to those obtained for 6H-SiC; power electronics applications currently favor the 4H polytype due to its higher electron mobility.

Fig. 4.1 Gate leakage current density as a function of temperature for 6H-SiC n-type devices. See Table 3.4 for details of the device geometry. The capacitor is biased at midgap to optimize device reliability at high temperature.

4.2 Time Resolved Sensor Measurements

We have developed a new technique for characterizing fast solid state planar gas sensors, as sensors with fast response times are required for monitoring and also controlling a variety of processes. Such characterization is difficult at the millisecond time scale in a conventional flow-thru cell, as the device responds to a mixture of two gases during the transition from one component to the next. Our experiments were motivated by the need for an experimental setup to measure sensor response times under *standard* industrial operating conditions, without resorting to extremely high gas flows [Gerblinger 1991] or using vacuum for fast transport of gas analytes to a surface [Kelleter 1992].

Using the moving gas outlets shown in Fig. 4.2.1, we are able to change the gas around the sensor from one component to the next within one millisecond in a step-like manner. By simultaneously sampling at 10kHz, 100Hz and 1Hz, we can capture the fast component of the sensor response as well as the steady state value in a single experiment. The rate of exchange of the gas around the sensor was quantified using Laser Induced Fluorescence (LIF) imaging. These measurements were made under standard industrial sensor operating conditions, including gas pressure and device temperature, while using flows typically found in a research laboratory. Since fast response times from planar gas sensors usually require elevated temperatures, we have included the ability to heat the device to 650 °C.

Fig. 4.2.1: Schematic of the fast gas sensor measurement apparatus. The sensor is mounted face down above one of the two gas outlets. The electrical actuator translates the moving gas outlets (MGO) by 2.3 mm in 2 ms, thereby switching the gas around the sensor from H₂ to O₂. [Ghosh 2005B]

Quantitative measurements of the gas exchange rate around the sensor were obtained from a temporal sequence of laser induced fluorescence images [Lozano 1992] taken in the x-z plane as shown in Fig. 4.2.2. The light intensity 0.1mm below the sensor position was determined as a function of time ($t=0$ is the beginning of the actuator pulse) for the both direction of motion of the MGO. The gas flow rate is 370 ml/min and the sensor to outlet separation is 1 mm. Under these conditions the gas environment of the sensor is completely exchanged in 1.22 ± 0.12 ms.

Fig. 4.2.2: Schematic of the laser induced fluorescence images of the MGO (a) at rest and (b) in motion. The gas outlets move sideways below the fixed sensor. The right gas flow is seeded with acetone, the left flow is not. By illuminating the space above the gas outlets with a UV laser pulse the acetone molecules luminesce and appear as bright areas in a photograph, while the gas flow on the left which is unseeded is dark. Quantitative information on the gas exchange rate is obtained by analyzing a series of digital images taken at a fixed time after the beginning of the electrical pulse to the actuator [Ghosh 2005B]

4.3 UHV Measurements of Sensor Response

Step response to hydrogen at fixed oxygen pressure

hydrogen response of gate #43 in the presence of fixed partial pressures of oxygen, has revealed three distinct regime: (i) hydrogen-deficient, in which there is significantly more oxygen than hydrogen, and water formation on the catalytic gate competes effectively with the sensing reaction; (ii) transition, in which the partial pressures are comparable and the sensor signal varies unusually strongly with hydrogen partial pressure, and (iii) oxygen-deficient, in which there is more hydrogen than oxygen and the effect of water formation is relatively minor. In the transition region the sensor signal varied with hydrogen partial pressure at a rate of ~ 800 mV/decade, much higher than in the other regimes.

Figure 4.3.1 displays a similar measurement on Gate #83 of the same device, at two different oxygen pressures. The same three regions are visible, and the enhancement of hydrogen sensitivity in the transition region is considerable. This gate does not have as

Figure 4.3.1. Sensor response in UHV to varying hydrogen pressure in the presence of a fixed oxygen background (shown by vertical dashed lines). As the gas mixture passes from hydrogen-deficient to oxygen-deficient, the sensor shows enhanced sensitivity to hydrogen, as high as ~ 220 mV/decade.

high sensitivity as Gate #43 in any of the regimes, but the qualitative behavior is similar.

4.4 UHV Sensitivity to hydrocarbons (propene) and CO

In order to characterize the device's sensitivity to hydrocarbons, we carried out UHV sensing measurements using the unsaturated linear hydrocarbon propene (C_3H_6). In Figure 4.4.1 we compare sensing measurements on Gate #83 to alternating pulses of (a) hydrogen and oxygen and (b) propene and oxygen. These measurements were made within a week of each other, and C-V curves measured concurrently were not significantly different. It is notable that the sensor response to propene is more than a factor of two larger than that to hydrogen, even though the nominal propene partial

Figure 4.4.1 UHV response of Gate #83 to a) hydrogen and b) propene (C_3H_6) at 527°C. For a given pressure the signal due to propene is significantly larger.

pressure was at least an order of magnitude lower than the hydrogen pressures used in (a). (As we discuss below, however, the actual propene partial pressure may have been considerably higher than the nominal pressure indicated by the residual gas analyzer.) Clearly the device exhibits strong sensitivity to hydrocarbons.

As Fig. 4.4.1(b) shows, the propene level remains high even after the leak valve is closed and oxygen is admitted to the chamber, presumably because the propene gas adsorbs on the walls of the chamber and is removed only over a period of hours. This persistently high propene level caused the sensor signal to rise strongly when the oxygen pressure was reduced at about 2500 s, even though no additional propene was admitted into the chamber. A small pulse of hydrogen at about 2700 s resulted in a further increase in the signal. Because of the persistence of propene in the chamber, it was not feasible to carry out a systematic quantitative study of the sensor response as a function of propene pressure in the absence of oxygen, as we have done for hydrogen.

Figure 4.4.2 shows the results of a set of propene response measurements carried out in the presence of a constant background pressure of oxygen, analogous to the hydrogen experiment shown in Fig. 4.4.1(a). Because of the long pump down time for propene, these measurements are very time-consuming, and it was possible to get only a few data points for each oxygen pressure. Nevertheless a few points are noteworthy. First, the sensitivity (slope of the curve) is ~ 3 times greater than for hydrogen, perhaps simply reflecting the larger number of hydrogen atoms per molecule for propene. Second, there appears to be a transition from a low-sensitivity to a high-sensitivity regime, similar to the response to hydrogen as the device passes from hydrogen-deficient to oxygen-deficient conditions. This behavior suggests that the surface chemistry of the hydrogen atoms is the same whether it is derived from hydrogen molecules or hydrocarbons, with

Fig. 4.4.2. Sensor response in UHV to varying propene pressure in the presence of a fixed oxygen background. As in the case of hydrogen, there is a transition to very high sensitivity with increasing propene pressure.

water formation competing with diffusion to the interface adsorption sites responsible for the sensing signal. For propene, however, the transition occurs at a nominal propene partial pressure roughly 100× lower than the oxygen partial pressure, instead of near the stoichiometric ratio of three oxygen molecules per propene molecule. This discrepancy suggests that the actual propene partial pressures may have been significantly higher than the residual gas analyzer signal suggests.

Accumulation of surface carbon due to propene exposure

The mechanism of hydrocarbon sensing presumably involves the catalytic dissociation of the molecule on the Pt gate, with the released hydrogen atoms migrating to bonding sites at the metal/oxide interface that give rise to the bias shift. It is important to determine what happens to the carbon backbone of the propene molecule. If the carbon remains on the surface, it could form a graphitic layer that would eliminate the catalytic activity of the gate. On the other hand, if it is readily oxidized, it may form carbon dioxide upon exposure to oxygen and desorb from the surface – heating in oxygen is in fact a standard technique for cleaning carbon from Pt surfaces.

Figure 4.4.3 shows a series of Auger spectra before, during and after propene sensing experiments. The top spectrum shows the gate after cleaning. As mentioned in section 3.1.2, it was no longer possible to remove all carbon and oxygen from the gate. The

Figure 4.4.3. Auger spectra of the Pt gate after cleaning, after exposure to propene gas at 527°C, and after several cycles of alternating propene and oxygen exposures, as in Fig. 4.4.1. Propene exposure increased the carbon concentration on the surface, and oxygen exposure only partially removed the carbon.

middle trace shows the sample after a single exposure to propene gas at 800 K (527°C). The most significant change is an increase in the carbon signal, indicating the deposition

of carbon on the surface. The bottom trace represents the state of the gate after a series of alternating propene and oxygen pulses, as in Fig. 4.4.1. The carbon level is reduced compared to the middle trace, but is still higher than before the propene and oxygen exposures. It should be remembered, however, that the propene level in the chamber remained relatively high even after the dosing valve was closed, so it is possible that some of the carbon seen in the bottom trace comes from the unintended exposure of the sample to residual background propene after the end of the last oxygen exposure.

Sensitivity to carbon monoxide

Silicon carbide field-effect sensors have been reported to show sensitivity to carbon monoxide [Nakagomi 1997, 2002]. It has not been clear, however, whether the response is caused directly by CO, or whether the CO reacts with ambient oxygen to change the device's response to low levels of ambient hydrogen. We have attempted to detect a response to CO, but the results, shown in Fig. 4.4.4, were inconclusive. When these measurements were made the sample had already experienced serious degradation, as described in section 3.1.2, and gate 43, on which the experiments reported above were carried out, was no longer usable. The experiment was instead conducted on Gate 41, which had not previously been thoroughly characterized, so its response to hydrogen, for example, was not well determined. Moreover the accumulation capacitance of this gate had decreased severely, from ~1000 pF to ~25 pF, so that noise and drift were significant problems. The figure shows some evidence of a response to CO, but the effect, even if real, is difficult to interpret because the hydrogen level also rose when CO was admitted, probably because of chemical reactions on the chamber walls or in the ion pump.

Figure 4.4.1 Attempt to measured sensor response to carbon monoxide, on Gate #41. There is some indication of a response to CO, but the measurement is inconclusive because of the poor signal to noise ratio, long-term drift, and the correlation of the hydrogen pressure with the CO pressure.

4.5.1 UHV studies of sulfur surface chemistry on the Pt gate

We have studied the deposition and removal of sulfur from the surface of the Pt gate in detail. Sulfur compounds, particularly hydrogen sulfide (H_2S) are common impurities in the gas flow for many applications, and sulfur is a notorious poison for transition metal catalysts. It is therefore important to determine whether sulfur can build up on the Pt gate, whether such buildup is detrimental to sensor performance, whether it is reversible, and what gas conditions can either prevent the buildup or remove the sulfur after it is deposited. A complete and quantitative description of the sulfur surface chemistry of these devices. [Kahng 2007].

Sulfur deposition in the presence of hydrogen and oxygen

In our earlier measurements we showed that sulfur would accumulate on the gate surface when the sample was exposed to H_2S at 800 K, even in the presence of hydrogen

or oxygen. Fig. 4.5.1 shows a more detailed investigation of this phenomenon. The ordinate represents, on a log scale, the sticking coefficient of sulfur (i.e. the probability that an incident hydrogen sulfide molecule will leave an atom of sulfur on the surface) normalized to its value at the lowest background pressures attainable in our system. To determine this value, the sulfur coverage was measured using AES before and after hydrogen sulfide exposure, as shown in Fig. 4.5.2, and the incident flux of hydrogen sulfide was calculated from the partial pressure and the time. If the surface is not saturated with sulfur, the ratio of these quantities is proportional to the sticking coefficient. If the surface is saturated, however, then the ratio gives only a lower limit to the sticking coefficient, since once the saturation coverage is reached, no further adsorption can occur. The horizontal bars with upward arrows in the figure represent such lower limits.

The abscissa is the background pressure of either hydrogen (squares) or oxygen during the H_2S exposure. Over the range of pressures studied, ambient hydrogen had no observable effect on sulfur adsorption. Oxygen strongly suppressed, but did not prevent, sulfur adsorption, reducing the sticking coefficient by nearly three orders of magnitude at an effective oxygen pressure of 10^{-4} Torr. Nevertheless, the surface could be easily saturated with sulfur within a few minutes.

All of the partial pressures studied here are of course far lower than the sensor would encounter in applications. The gas *ratios*, however, were chosen to be more realistic, with $\text{H}_2:\text{H}_2\text{S}$ or $\text{O}_2:\text{H}_2\text{S}$ ratios ranging from ~ 1 to $\sim 10^3$. For comparison, 200 ppm of H_2S in a 20% H_2 atmosphere would be a ratio of 10^3 .

Fig. 4.5.1. Normalized sticking coefficient of sulfur from H_2S as a function of background pressure of oxygen or hydrogen. The horizontal bars represent lower limits, since in these cases the sulfur coverage reached saturation. Hydrogen has no observable effect on sulfur adsorption, but oxygen suppresses it by at least three orders of magnitude over the pressure range studied.

Fig. 4.5.2. Comparison of Auger signals from clean and sulfur-contaminated Pt gate. The ratio of the amplitudes of the 152 and 237 eV peaks is used as a linear measure of sulfur surface coverage.

Oxygen cleaning kinetics

Our previous measurements showed that adsorbed sulfur could be completely removed by exposure of the sample to oxygen at 800 K. When the sulfur coverage was relatively low, the cleaning was very fast. When the surface was nearly saturated with sulfur, however, the cleaning proceeded much more slowly. We have investigated this phenomenon in more detail, varying the sulfur coverage, oxygen pressure and exposure time.

The results are summarized in Fig. 4.5.3. The ordinate (log scale) is the reaction coefficient, which represents the average number of sulfur atoms removed from the surface per incident oxygen molecule. In order to determine this quantity, the sulfur coverage is determined both before and after oxygen exposure, using Auger spectroscopy. The flux of oxygen molecules at the surface is calculated from the oxygen partial pressure (including the doser enhancement factor) and the exposure time. Because of uncertainties in calibration, the absolute values could be off by as much as a factor of two, but relative values are much more accurate, as indicated by the error bars. The horizontal bars are lower limits; in these cases the sample was completely clean of sulfur after oxygen exposure, so we can only set a lower limit on the reaction rate.

At low sulfur coverage, the removal process is very efficient; extrapolating to zero coverage gives a reaction coefficient close to unity. With increasing sulfur coverage, however, the rate falls off rapidly – nearly exponentially – dropping to a reaction

probability $\sim 10^{-4}$ at the highest coverages studied. Even at that low rate, however, the surface could be completely cleaned in a matter of minutes at an oxygen partial pressure $\sim 10^{-4}$ Torr.

These results are qualitatively consistent with previous experiments on platinum single crystals [Bonzel 1973A, Bonzel 1973B, Astegger 1982, Köhler 1984]. The sulfur removal reaction is a Langmuir-Hinshelwood process (i.e. a reaction between adsorbed species on the surface) comprising the following steps:

where the notations (a) and (g) denote adsorbed and gas-phase species, respectively. At high coverages, sulfur blocks the adsorption sites, preventing oxygen from dissociating and thereby inhibiting the reaction. Köhler et al. found that the sticking coefficient of oxygen on Pt(111) went to zero for sulfur coverages above 0.09 ML. Sulfur oxidation was observed even at much higher coverages, however, because of a small residual oxygen adsorption rate on open Pt sites that arise from statistical fluctuations in the sulfur overlayer. All workers agree that the sulfur oxidation rate is drastically reduced for sulfur coverages above about 0.25 ML. Our results show that these trends are maintained on the much more complex surface of our activated gates.

Fig. 4.5.3. Reaction coefficient (S atoms removed per incident O₂ molecule) for a S-precovered gate exposed to oxygen gas at 800 K, as a function of the initial S coverage in monolayers (ML). For the data indicated by squares, hydrogen gas was also introduced at a level of 7×10^{-7} Torr.

4.6 Industrial Sensor Measurements

The goal of our experiments in this phase of the project was to demonstrate the viability of using our SiC sensor to monitor hydrogen concentration under a variety of industrial conditions, including combustion of fossil fuels and fuel reforming [Loloe 2007].

June 2005

The measurements were performed in the B-# reactor at NETL, with the sensor temperature fixed at 600 C, the gas temperature was between 350 -370 °C and the gas flow was ~1000 sccm. Shown in Fig. 4.6.1 is sensor sensitivity as a function of hydrogen concentration (over 2.5 decades). We demonstrated a hydrogen sensitivity of 220 mV/decade for 0.1% - 50% H₂ (T_{gas} = 350°C) @ a flow ~ 1000 sccm with a T_{sensor} = 600°C. These results were validated with the on-line mass spectrometer data shown in Fig. 4.6.2

Fig 4.6.1 Sensor sensitivity (ΔV) as a function of hydrogen concentration from a 1 mm gate from chip SiC-II+I mounted in NETL test unit #1 in the B-3 micro-reactor at NETL. The sensor temperature was 600C, and the gas was 350 C at flow rate of 1000 sccm. 1% O₂ was used as the base gas.. The device sensitivity is 256 mV/decade.

Fig 4.6.2 . Validation of the SiC hydrogen sensor measurements with mass spectrometer data. Plotted is the data from Fig. 4.6.1 along with the H₂ and O₂ mass spec signal

. Shown in Fig. 4.6.3 are the effects of “standard” interferents, CH₄ (5%) CO (40%) and CO₂ (40%) on a 20% H₂ flow at 1000 sccm, with a gas temperature of 350 C. The lower portion of the figure shows both the mass spectrometer and SiC sensor response to the gas mixtures. Starting in a 20% hydrogen flow (signal magnitude ~1.2V) we first added 5% CH₄ at time=3000 s. No effect was observed on the sensor signal. Five hundred seconds later, 40% CO₂ was added to the gas flow, resulting in a 90mV positive (oxidizing) response. At time=4000s, 40% CO was added, no response was observed except for a 5mV discontinuity, which we attribute to a sudden increase in the hydrogen concentration, per the mass spec signal. At this point methane followed by carbon monoxide were removed, resulting in no change of the sensor signal. Upon removal of carbon dioxide the sensor signal decreased by 90mV, i.e. returning to the original reducing signal.

We conclude that for a 20% hydrogen flow, methane and carbon monoxide have a negligible effect on the hydrogen sensitivity of the SiC sensor. Carbon dioxide, has a small, ~6% effect.

Fig. 4.6.3 Hydrogen sensor performance under “typical” fuel reforming conditions. Shown is the effect of “standard” interferents, CH₄, CO₂ and CO on a 20% H₂ flow at 1000 sccm ($T_{\text{gas}} = 350\text{ }^{\circ}\text{C}$) and a sensor temperature of 600 °C.

The goal of our experiments was to test the sensitivity of our SiC sensor as a hydrogen monitor in simulated syngas mixtures based on the typical composition reported by Tampa Electric Company's Polk Power Station. Hydrogen, carbon monoxide, and carbon dioxide were varied to simulate possible syngas composition fluctuations. In consultation with Susan Maley we identified typical stream compositions and conditions for potential applications for our SiC based hydrogen gas sensor. These include monitoring the gas stream in a syngas application and in the "Cold gas cleaning process" of integrated gasification combined cycle (IGCC) gasifiers.

Syngas production from coal, which is then cleaned and used as fuel gas in a combined cycle power turbine, takes place in an integrated gasification combined cycle (IGCC) power plant. For optimal operation, however, use of syngas in advanced power production will require online monitoring of the syngas composition. SiC based gas sensing measurement systems (gas sensors) are good candidates for reliable measurements in the harsh and chemically corrosive operating conditions found within the coal gasifier. Other potential applications for SiC n-MOS gas sensor include monitoring the syngas fuel gas flow to a turbine or high temperature fuel cell. Table 4.6.1 lists the typical stream composition from: (i) the Cold-Gas Clean-up Zone for an IGCC gasifier, (ii) six different of fuel cells and (iii) a natural gas exhaust stream from several different power plants.

Table 4.6.1

Composition	Fuel gas composition for Destec Gasifier IGCC; Cold gas cleaning	Coal Gas composition 6 sources from Fuel cell CD	Natural gas Fuel Pressurized PAFC (Anode Exhaust)
CH ₄	800 ppm-0.1%	0.1-4.6%	9%
H ₂	24-39%	16.1-33.9%	29%
CO ₂	5-9%	1.5-15.5%	51%
CO	31-50%	5.8-63.1%	2%
O ₂	0-0.2%	-	-
H ₂ S	47 – 75 ppm	0.2-1.3%	-

Effect of common "interferants" – CO, CO₂ and CH₄ on hydrogen sensor performance

The purpose of this experiment is to check the sensitivity of our sensor in selected syngas mixes at 250-500 °C with 300-1000 sccm gas flow without H₂S or water vapor in the system. In Fig. 4.6.4 the sensor was initially presented with the following gas streams: 1 %O₂, 37% hydrogen, 1 % oxygen, then mix 61, 64, and 68, where the hydrogen concentration was kept constant while varying the CO and CO₂ values every seven minutes intervals. Following the initial 1000 mV response to 37 % H₂ from the 1 % O₂

baseline, the sensor signal is essentially flat. This indicates that the SiC sensor response to hydrogen is not significantly perturbed by varying either the CO or CO₂ levels,

Fig.4.6.4 Performance of the SiC sensor under “typical” fuel reforming conditions. The lower trace is SiC sensor response to 1% O₂ followed by gas mix 61, 64, 68. The upper trace is in-line mass spectrometer signal of the gas composition inside the measurement chamber. The numbers in the inset to the lower trace are from the mass spec data.

Effect of long-term exposure to H₂S on sensor performance

The presence of sulfur species creates a challenge for monitoring coal-based combustion processes. Specifically devices with refractory metal catalytic sensing films such as platinum, can be poisoned by H₂S. In this experiment we inserted different doses of H₂S into selected syngas mixtures. Both the sensor response and the behavior of capacitance voltage (CV) were monitored to assess the effect of sulfur.

Fig.4.6.5 Performance of the SiC sensor in a “typical” fuel reforming conditions in the presence of sulfur. The lower trace is SiC sensor response to gas mix 92, 94, 96, and 99. The upper trace is in-line mass spectrometer signal of the gas composition inside the measurement chamber. The numbers in the inset to the lower trace are from the mass spec data. The data were taken on 11/1/06.

Table 4.6.2
H₂S levels for the data in Fig. 4.2.3.2 (for 11/1/06)

	Mass Spectrometer – post processed average over 7 minutes (ppm)	Gas Chromatography outlet gas grab (ppm)
Mix 92	15	48.5
Mix 94	22	78.8
Mix 96	28	68.9
Mix 99	37	91.9

It is instructive to compare the data in Figs. 4.6.5 with a previous sequence of syngas mixtures, except that the second data sets include sulfur. The H₂S level rises from 48 to 92 ppm from the first to the last gas mixture. Aside from a 50 mV vertical shift the two measurement sets are identical with the signal to noise ratio. Therefore we can conclude that at the 48 – 92 ppm level, H₂S has no adverse effect on the performance of the SiC sensor as a hydrogen monitor in a simulated syngas mixture.

The data indicates that if we fix the hydrogen concentration to around 37%, addition of CO (31-46 %), CO₂ (14 %), CH₄ (1%) and H₂S (50 - 100 ppm) modifies the sensor output by only a few percent. To confirm these results we measured the capacitance-voltage characteristic of the SiC sensor in (i) 37 % H₂, (ii) Mix 61 and (iii) Mix 81*. Note that for Mix 81* the H₂S level is 286 ppm as measured by an outlet gas grab. The sensor setpoint was chosen to be between 320-350 pF. The C-V characteristic in this region for all three gas mixtures lie on top of each other, confirming the fact that the sensor response to hydrogen will not be affected by the interferants or up to 280 ppm of H₂S. Note that at this point the sensor has been exposed to four cumulative hours of sulfur exposure as discussed below.

At this point the SiC sensor has been exposed to syngas mixes containing sulfur for a total of about 8 hours. During this period the minimum H₂S level was 650 ppm, as measured at the outlet of the sensor module, and a maximum H₂S level was 940 ppm as measured at the inlet to the sensor module. To determine if the SiC sensor still responded to hydrogen, we measured the sensor sensitivity as a function of hydrogen concentration. The data are given in Fig. 4.6.6 (blue triangles). The gas temperature was 370 °C with a flow rate of 1000 sccm, while the SiC sensor itself was heated to 600 °C. The device sensitivity prior to any sulfur containing syngas exposures are given by the red circles. We obtain a logarithmic response for the measurements for both before and after exposure to H₂S, and a least squares linear fit to the data from yields:

$$\begin{array}{lll} Y = 0.8972 + 0.1198 \log(x) & R = 0.9973 & \text{(before H}_2\text{S)} \\ Y = 1.06 + 0.112 \log(x) & R = 0.992 & \text{(after H}_2\text{S)} \end{array}$$

The magnitude of the sensor response actually increases after sulfur exposure while the sensitivity decreases from 120 to 112 mV/decade. These results are a clear demonstration that the SiC sensor is healthy and not poisoned by exposures as high as 740 ppm of H₂S for several hours.

Fig. 4.6.6. Sensor sensitivity before and after exposure to H_2S as a function of hydrogen concentration. The device sensitivity is 120 mV/decade before and 112 mV/decade after 8 hours of exposure to H_2S .

Effect of long-term exposure to H_2S and H_2O on catalyst morphology and sensor packaging

Following 8 days of measurements in the harsh industrial environment of a syngas stream which included H_2S and water vapor in the Catalyst Screening Unit at NETL, Morgantown the physical appearance of the sensor chip was examined upon its return to MSU. We observed a large amount of debris all over the sensor chip and header, including on top of the Pt gates and on the gold wire bonding pads. Most of the gold wires, which were bonded to the surface of Pt gates and the gold pads on the alumina header, appeared to have been etched. These wires eventually collapsed on top of each other causing electrical short circuits between the gates and ground. Photos of the sensor chip itself and the chip mounted inside sensing module #1, prior to the measurements on Oct – Nov 2006 at NETL are shown in Fig. 4.6.7a and 4.6.7b respectively. The amount of deposits and physical damage to the sensor and alumina header due to exposure to syngas mixtures containing- H_2S and H_2O at high temperature are shown in Fig. 4.6.8. Chemical analysis of the debris is in progress to determine its origin. The debris does not appear to be soot.

Next Page:

Fig. 4.6.7 Photograph of the sensor chip (a) and the chip mounted in module #1 (b) prior to measurements in a simulated syngas environment.

Fig. 4.6.8 Photographs of the sensor chip and holder after 8 days of measurement in simulated syngas at NETL.

Fig. 4.6.7a

Fig. 4.6.7b

Fig. 4.6.8a

Fig. 4.6.8b

Fig. 4.6.8c

Fig. 4.6.8d

Hydrogen sensitivity of Pt gates after repair of electrical leads

In order to determine if the sensor chip was still functional we decided to repair the physical damage to device 85 from which we had collected data at NETL for 8 days.. We removed any deposits and collapsed electrical leads that were causing shorts and strengthened the Au lead bonded to the gate with Ag paint. This allowed us to measure the device C-V characteristic again, so the sensitivity of this device was then checked by exposing the sensor to 1%O₂ and 29.2%, 9.73%, 0.984%, 0.201%, 0.052%, & 0.0053% H₂; respectively. The data are given in Fig. 4.6.9. The sensor is most definitely not dead! As all our sensors it has a logarithmic response to hydrogen. The data from the same device prior to measurements at NETL are also shown. A least squares linear fit to the data yields:

$$Y = 0.9487 + 0.3326 \log(x) \quad R = 0.9969 \quad (\text{after syngas exposure at NETL})$$

$$Y = 0.6543 + 0.05648 \log(x) \quad R = 0.9998 \quad (\text{before syngas exposure})$$

Fig. 4.6.9. Sensor sensitivity as a function of hydrogen concentration for a 1 mm gate (device 85) from chip SiC+I-I mounted in NETL test unit #2 at MSU. i) red squares - prior to syngas exposure at NETL and ii) blue circles – following syngas exposure at NETL. The sensor temperature was 600 °C, with a 60 sccm gas flow at 24 °C. 1% O₂ was used as the base gas. The device sensitivity has changed by a factor 6 from 56 to 332 mV/decade.

The slope or sensitivity of the device increased by a factor 6 due to further activation of the Pt sensing film in high temperature gas (370 °C) from 56 to 332 mV/decade. In addition the absolute value of the sensor signal increased as well. These results confirm our suspicion that the erratic electrical behavior observed during the combined water and sulfur exposure was due failure of the Au wires. One potential solution is to use Pt wires instead, as the Pt gates themselves show to signs of etching. The data in Fig. 4.6.9 clearly demonstrate that in no way is our Pt/SiO₂/SiC sensor poisoned by exposure to both water and concentrations of H₂S as high as 740 ppm for several hours.

4.7 Effect of activation and high temperature gas on sensor morphology and structure

Surface temperature of the Pt catalyst in hot syngas environment

In order to reliably monitor the hydrogen concentration in a simulated syngas environment with our SiC sensor it is necessary to accurately know the temperature of the Pt catalyst. We find that the SiC sensor surface is consistently (49 ± 1) °C cooler than the backside Pt heater. We used this fixed temperature offset for all the sensing measurements in the catalyst screening unit. In Fig. 4.7.1 we show that the heater power needed to maintain the SiC sensor at a fixed temperature of 600 °C as a function of hydrogen concentration. A least squares fit to the data yields:

$$\text{Joule heating (W)} = (6.073 \pm 0.034) + (0.0268 \pm 0.0010) * (\text{H}_2\%)$$

From these experiments we postulate that the catalytic process at the Pt sensing film responsible for hydrogen transduction is a dynamic process dependent on the kinetic energy of the hydrogen gas through the gas temperature and flow rate. The thermometry measurements provide insight into the physical mechanisms involved in hydrogen transduction.

Figure 4.7.1 I²R heater power required to maintain the Pt sensing film at 600 °C as a function of hydrogen concentration. The gas temperature is 483 °C and the gas flow rate is 1000 sccm.

Syngas production from coal, which is then cleaned and used as fuel gas in a combined cycle power turbine, takes place in an integrated gasification combined cycle (IGCC) power plant. For optimal operation, however, use of syngas in advanced power production will require online monitoring of the syngas composition. SiC based gas sensing measurement systems (gas sensors) are good candidates for reliable measurements in the harsh and chemically corrosive operating conditions found within the coal gasifier. Other potential applications for SiC n-MOS gas sensor include monitoring the syngas fuel gas flow to a turbine or high temperature fuel cell. Table 4.7.1 lists the typical stream composition from: (i) the Cold-Gas Clean-up Zone for an

IGCC gasifier, (ii) six different of fuel cells and (iii) a natural gas exhaust stream from several different power plants.

Table 4.7.1

Composition	Fuel gas composition for Destec Gasifier IGGC; Cold gas cleaning	Coal Gas composition 6 sources from Fuel cell CD	Natural gas Fuel Pressurized PAFC (Anode Exhaust)
CH ₄	800 ppm-0.1%	0.1-4.6%	9%
H ₂	24-39%	16.1-33.9%	29%
CO ₂	5-9%	1.5-15.5%	51%
CO	31-50%	5.8-63.1%	2%
O ₂	0-0.2%	-	-
H ₂ S	47 – 75 ppm	0.2-1.3%	-

The following Pt sensing films were characterized by optical microscopy, XRD, XPS, AFM and TEM:

- i) *As Deposited Film* --- has not been exposed to any heat treatment or gases.
- ii) *Activated Film tested in Industrial Reactor (Morgantown)* --- After routine activation at RT gases and 30 hours of operation at NETL-Morgantown reactor with gas temperature of 350 °C and substrate temperature of 620 °C and additional 18 days of post operation at RT gases at MSU laboratory.

Optical Images

Bright Field images are convenient to demonstrate the surface morphology of the shiny and smooth Pt gates before activation. However, Dark Field images of smooth and shiny surfaces are featureless, but provide an excellent way to bring out the texture from rough surfaces created during the activation process. For the samples which were exposed to high temperature gas either at NETL-Morgantown reactor (Industrial Reactor) or at MSU-nano-reactor (Lab Reactor), both BF and DF images appear the same. The left hand side image shown in Fig. 4.7.2 is the BF images of 1000 μm and 500 μm gates and on the right hand side, the DF images from the same area of *non-activated gates* are illustrated.

Fig. 4.7.2. High magnification micrographs of a few Pt gates before activation. The left image shows the BF image of the gates and the right image shows the DF image of the same gates. As the Pt surface is mirror smooth and shiny prior to activation, the DF image is featureless.

ii) Activated Film tested in Industrial Reactor (Morgantown) --- After routine activation at RT gases and 30 hours of operation at NETL-Morgantown reactor with gas temperature of 350 °C and substrate temperature of 600 °C and additional 18 days of post operation at RT gases at MSU laboratory.

Fig. 4.7.3. Bright field images of one of the device which was operated in an industrial reactor (Morgantown). On the top left the image of the whole device (1.25X) and on the upper right magnified image of 4 gates (5X). On the lower left portion of same gate with 20 X magnifications and on the lower right increased the magnification to 100X.

Atomic Force Microscopy images

The AFM images are collected from same five sets of samples which optical images were collected:

- i) Activated Film tested in Industrial Reactor (Morgantown) --- After routine activation at RT gases and 30 hours of operation at NETL-Morgantown reactor with gas temperature of 350 °C and substrate temperature of 600 °C and additional 18 days of post operation at RT gases at MSU laboratory.

Fig. 4.7.4. AFM images of a 1000 μm Pt gate of device 6H-SiC7-II+I, after 8 hours of activation at room temperature gas and substrate temperature of 600 °C and then 40 hr of operation at 350 °C in an industrial reactor. The images on the top are from 5 μm x 5 μm (Image Z range: 400nm) including the surface roughness along a horizontal line and on the bottom from 20 μm x 20 μm (Image Z range : 300nm) scanned area.

X-ray Photoelectron Spectroscopy

XPS depth profiles of a number of samples were obtained. Shown in Fig. 4.7.5 is a Pt 4f image of 1000 μm diameter Pt sensing film. The dark spot is the hole left over after removal of the bond wire. These images were used to precisely position the 110 μm micro-spot to obtain high resolution XPS spectra,

Fig. 4.7.5 Pt 4f image of a 1000 μm diameter sensing film.

Activated Film post laboratory (MSU)-Reactor

Fig. 4.7.6 shows the spectra from a sensor that was tested for an extended period of time in the laboratory reactor. Compared to the activated film the Pt signal intensity is reduced by a factor of two and also extends significantly deeper into the sample. Si is present through out the depth that was probed.

Fig. 4.7.6 Sputter depth profiling of a sensing film following extended testing in a laboratory reactor.

X-ray Diffraction

The structure of the Pt gates of all five sets of devices was investigated by collecting x-ray diffraction (XRD) patterns from each set. The XRD patterns from Pt gates of two samples are shown in Figures 4.7.7 and 4.7.8. As seen in all figures only the Pt (111) peak at $2\theta \cong 39.7^\circ$ is observed and the Pt (002) peak at $2\theta \cong 46.2^\circ$ was not seen. This indicates that the Pt film is textured Pt (111) and remained the same regardless of history of the devices. In the XRD patterns collected from these devices two or three peaks (1-3) appeared with Pt (111) (#2 at $2\theta \cong 39.7^\circ$) as the dominant peak. The spectrum has a higher background below 39.7° , suggestive of an amorphous material on the surface. There are two additional small peaks, (1) at $2\theta \cong 38^\circ$ and (3) at $2\theta \cong 44^\circ$. The lattice parameters of peaks 1 & 3 (see Table 4.7.2) do not match the first or higher order orientations of Pt, PtO and PtO₂. Note that some of the devices had Gold back metallization and also most gates had a bonded Au wire (or residual Au wire). The Au (111) peak is at $2\theta \cong 38.11^\circ$ and the (002) peak is at $2\theta \cong 44.29^\circ$, therefore we attribute peaks 1 and 3 to residual gold from the wire bonding processes or from the back Au film.

(h, k, l)	Pt- d_{hkl} (Å) $\leftrightarrow$ 2θ	PtO- d_{hkl} (Å) $\leftrightarrow$ 2θ	PtO ₂ - d_{hkl} (Å) $\leftrightarrow$ 2θ
001	----	----	4.342 $\leftrightarrow$ 20.43°
100	----	3.077 $\leftrightarrow$ 29°	2.696 $\leftrightarrow$ 33.19°
002	1.962 $\leftrightarrow$ 46.2°	2.670 $\leftrightarrow$ 33.52°	2.171 $\leftrightarrow$ 41.54°
101	----	2.666 $\leftrightarrow$ 33.57°	----
110	----	2.176 $\leftrightarrow$ 41.45°	1.556 $\leftrightarrow$ 59.32°
111	2.266 $\leftrightarrow$ 39.73°	----	1.465 $\leftrightarrow$ 63.42°
200	----	1.538 $\leftrightarrow$ 60.08°	1.348 $\leftrightarrow$ 69.67°
202	1.387 $\leftrightarrow$ 67.44°	1.333 $\leftrightarrow$ 70.57°	---

Table 4.7.2 X-ray diffraction parameter for Pt, PtO and PtO₂ from [EMC] and [McBride 1991].

- i) Just Activated Film --- has been exposed to room temperature 0.005% - 10% H₂ and 1% O₂ gases with substrate at 600 °C for 4-6 hours.

Fig. 4.7.7 X-ray diffraction scans of Pt sensing layers deposited on oxidized SiC. The data shows that the Pt layers are highly textured (111) films (Peak #2) and small peak from residual gold bonded wire on the gates (peak#1 & #3).

- ii) Activated Film tested in Industrial Reactor (Morgantown) --- After routine activation at RT gases and 30 hours of operation at NETL-Morgantown reactor with gas temperature of 350 °C and substrate temperature of 600 °C and additional 18 days of post operation at RT gases at MSU laboratory.

Fig. 4.7.8 X-ray diffraction scans of Pt sensing layers deposited on oxidized SiC. The data shows that the Pt layers are highly textured (111) films (Peak #2) and small peak from residual gold bonded wire on the gates (peak #3).

TEM of the as-deposited sample (for example Fig. 4.7.8) revealed a well-defined single crystal SiC substrate, a continuous light contrast amorphous layer approximately 40 nm thick (consistent with SiO₂), and a dark contrast continuous columnar polycrystalline layer approximately 80 nm thick, consistent with the Pt. On top of this dark polycrystalline layer is a much lighter contrast polycrystalline layer, consistent with the lighter Z of Nb.

Fig. 4.7.8. TEM-cross sectional viewgraph of “As Grown sample”. There are a smooth interfaces between “SiC - SiO₂ - Pt”. The continues columnar polycrystalline nature of Pt film is clearly observable. The top cover of Nb film was deposited only for TEM-FEB processing.

Activated Film tested in Industrial Reactor (Morgantown) --- After routine activation at RT gases and 30 hours of operation at NETL-Morgantown reactor with gas temperature of 350 °C and substrate temperature of 600 °C and additional 18 days of post operation at RT gases at MSU laboratory.

Following the operation in Industrial Reactor environment, significant morphological changes were noted in the devices. Most striking is the change in the appearance of the Pt to a much more rounded islanded morphology, with significant pin-holes (Fig. 4.7.9).

Fig.4.7.9. TEM-cross sectional viewgraph of “Sample Operated in Industrial reactor Environment”. There is still a smooth interface between “SiO₂ – Pt”. However, a rough (rounded) surface morphology and existence of pinholes are clearly observable.

5. CONCLUSION

We have developed Pt/SiO₂/SiC capacitive sensor for detection of hydrogen containing species and demonstrate that the device can be used as a hydrogen monitor in syngas applications in the presence of common interferants as well as sulfur and water vapor. These measurements were made NETL, Morgantown under atmospheric conditions. The sensor response to hydrogen gas at 350 °C is 240 mV/decade, this is significantly higher than the device response to room temperature gas or that predicted from vacuum chamber studies. The enhanced catalytic activity of the platinum sensing film under energy plant operating conditions was investigated via AFM, x-ray diffraction, TEM and x-ray photoelectron spectroscopy. Our characterization indicated that exposure to high temperature gases significantly modifies the morphology of the Pt catalytic film and the Pt/SiO₂ interfacial region, which we tentatively attribute to the enhanced hydrogen sensitivity of the sensing film. A model for the hydrogen/oxygen response of the SiC device under atmospheric conditions was developed. It is based on two independent phenomena: a chemically induced shift in the metal-semiconductor work function difference and the passivation /creation of charged states at the SiO₂-SiC interface. The optimum operating set point for the SiC sensor with respect to response time and long term reliability was determined to be close to mid-gap.

Ultrahigh vacuum (UHV) techniques were used to investigate the effects of sulfur contamination on the Pt gate. Exposure to hydrogen sulfide, even in the presence of hydrogen or oxygen at partial pressures of 20-600 times greater than the H₂S level, rapidly coated the gate with a monolayer of sulfur. Although hydrogen exposure could not remove the adsorbed sulfur, oxygen was effective at removing sulfur with no evidence of irreversible changes in device behavior. The role of oxygen in the functioning of the SiC sensors was also investigated. All of the results are consistent with oxygen acting through its surface reactions with hydrogen, including the need for oxygen to reset the device to a fully hydrogen-depleted state and competition between hydrogen oxidation and hydrogen diffusion to metal/oxide interface sites. A strong sensor response to the unsaturated linear hydrocarbon propene (C₃H₆) was observed.

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None

LIST OF ACRONYMS AND ABBREVIATIONS

SiC – silicon carbide

SiO₂ – silicon dioxide

MISiC – metal insulator silicon carbide (device)

Quasi-static – calculated C-V from the charge flowing onto a sensor at each voltage step

TPD – temperature programmed desorption

QMS – quadrupole mass spectrometer

AES – Auger electron spectroscopy

UHV – ultra high vacuum

PID – proportional-integral-derivative