Low-power catalytic gas sensing using highly stable silicon carbide microheaters

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Abstract

A robust silicon carbide (SiC) microheater is used for stable low-power catalytic gas sensing at high operating temperatures, where previously developed low-power polycrystalline silicon (polysilicon) microheaters are unstable. The silicon carbide microheater has low power consumption (20 mW to reach 500 °C) and exhibits an order of magnitude lower resistance drift than the polysilicon microheater after continuously heating at 500 °C for 100h and during temperature increases up to 650 °C. With the deposition of platinum nanoparticle-loaded boron nitride aerogel, the SiC microheater-based catalytic gas sensor detects propane with excellent long-term stability while exhibiting fast response and recovery time (~1 s). The sensitivity is not affected by humidity, nor during 10% duty cycling, which yields a power consumption of only 2 mW with frequent data collection (every 2 s). With a simple change of heater material from silicon to SiC, the microheater and resulting catalytic gas sensor element show significant performance improvement.

Keywords: gas sensor, silicon carbide, microheater, catalytic gas sensor, boron nitride aerogel, combustible gas

(Some figures may appear in colour only in the online journal)

1. Introduction

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

The main reason for the high power consumption of the current sensor components is the need for the catalyst to be heated to high temperatures (~500 °C). To minimize the power consumption, two main strategies have been proposed: (1) miniaturization through the use of microfabricated heaters, and (2) reduction of the combustion temperature. Research efforts on efficient low-temperature hydrocarbon combustion...
The back-side of the wafer to expose the silicon substrate, which is anisotropically etched with hot KOH to release the membrane.

Window in the top LSN layer, Pt/Ti metal contacts are created through photolithography, evaporation, and lift-off. (h) A window is etched in and plasma etched to form the microheaters. (f) Deposition of a second LSN layer encapsulates the microheaters. (g) After etching a of a low-stress silicon nitride (LSN) layer and doped polycrystalline silicon carbide layer. (e) polySiC is patterned with photolithography powered to glowing, showing hot zone. (d) Low pressure chemical vapor deposition of a low-stress silicon nitride (LSN) layer and doped polycrystalline silicon carbide layer. (c) polySiC is patterned with photolithography and plasma etched to form the microheaters. (f) Deposition of a second LSN layer encapsulates the microheaters. (g) After etching a window in the top LSN layer, Pt/Ti metal contacts are created through photolithography, evaporation, and lift-off. (h) A window is etched in the back-side of the wafer to expose the silicon substrate, which is anisotropically etched with hot KOH to release the membrane.

have not yielded promising results [1, 2]; thus research focus has been on the use of microheaters as the catalytic gas sensor platform [3–6]. A microfabricated sensor platform can leverage silicon micromachining processes for low cost and reproducible manufacturing. Microheaters have been fabricated from a variety of materials, most commonly polysilicon or platinum, and consist of a heater trace thermally isolated from the substrate via a thin membrane of silicon nitride or silicon dioxide. Joule heating is used to reach the desired operating temperatures.

Although progress has been made in minimizing the power consumption of these microheaters, deployment of microheater-based catalytic gas sensors is contingent on obtaining stable, reproducible measurements in field conditions. Platinum and polysilicon microheaters both suffer from instability when operated at the high temperatures required for catalytic gas sensing. Platinum suffers from electromigration, poor adhesion to the most common membrane materials [7, 8], and oxidation if it is not isolated from the atmosphere. The resistance of polysilicon is not very stable as it approaches the recrystallization temperature (~600 °C [9]), where grains can coalesce and cause long-term drift [10–12]. Especially considering that 500 °C is the baseline operating temperature and the temperature increases in the presence of combustible gas, these materials suffer from severe drawbacks for long-term use.

Silicon carbide has been investigated as an advantageous material for microelectronics and microsensors involving high temperature operation [13, 14]. The robust performance of silicon carbide at high temperature makes it an attractive replacement for polysilicon [13]. Silicon carbide has been used in microheater fabrication, both as a membrane material since its high thermal conductivity leads to better temperature uniformity across the device [15–19], and as the microheater material itself [14, 16, 20–23]. SiC microheaters have demonstrated robust behavior in high temperature applications [14, 23], including for metal oxide-based gas sensing [16, 17], but their use for catalytic gas sensing is not reported to-date.

In this paper, we report the development of a low-power silicon carbide microheater, requiring only 20 mW to reach 500 °C [24, 25]. Comparison of the SiC microheater to a polysilicon microheater with the same dimensions shows significant improvements in baseline resistance stability for operation at 500 °C and above. With the integration of an advanced catalytic material, platinum nanoparticle-loaded boron nitride aerogel, the SiC microheater platform can be used for propane detection with high sensitivity, fast response and recovery (~1 s) and highly stable response. Additionally, the sensitivity is unaffected by humidity and 10% duty cycling, so the power consumption can be decreased to only 2 mW with data still collected every 2 s. These developments offered by the silicon carbide microheater can unlock the true potential of low power catalytic gas sensing for wireless applications.

2. Materials and methods

2.1. Microheater fabrication

The microheater platform consists of a back-etched silicon nitride membrane encapsulating four microheater elements on a single chip that is 3.5 × 3.5 mm² in size (figure 1(a)). The thin membrane provides the microheaters with thermal isolation from the substrate to keep the power consumption low requiring only 20 mW to reach 500 °C. Because the silicon
nitride layers are optically transparent, the encapsulated SiC trace (pink) can be seen in figure 1(b). The two Pt/Ti sensing electrodes (white) are not used in this work and are masked with a thin layer of silicon dioxide before sensor testing to avoid interference from the platinum. Figure 1(c) shows an optical image of the microheater powered to the point where it is glowing, which shows that the hot zone is the thinnest part of the trace, giving an approximately 50 × 50 μm² heated area. Figure 1 shows a cross-sectional schematic of the microheater with the closed membrane configuration and metal contacts placed off the membrane to keep them cool and hence, avoid stability issues associated with metal contacts at elevated temperatures. The closed membrane assists with integration of the sensing material by providing a flat surface for deposition.

The silicon carbide fabrication process follows the previously developed polysilicon microheater fabrication, described in detail elsewhere [24, 26]. To facilitate comparison, only the deposition and etch chemistries for the silicon carbide steps are changed. Briefly, the deposition of a 100nm low-stress silicon nitride (LSN) layer on a 4 inch p-type double-side polished silicon wafer is followed by the silicon carbide film deposition (figure 1(d)). The SiC film is deposited using methylsilane, hydrogen, and dichlorosilane as precursors in a low-pressure (170 mTorr) hot-wall reactor at \( T = 835 \) °C with a dopant source of ammonia gas and with the wafers in a closed-boat geometry with slots to limit the gas diffusion and improve the film uniformity [27]. The deposited film is polycrystalline cubic 3C-SiC with a sheet resistivity of 5700 Ω/square and a thickness of 130nm. To define the microheaters (figure 1(e)), the wafer is patterned with photolithography employing positive photoresist (FujiFilm OiR 906-12) with a thickness of ~1.2 μm as the mask. To selectively remove the SiC, reactive ion etching is done with HBr and Cl₂ gases using a transformer coupled plasma system [28]. A high power of 300 W is needed to have an appreciable etch rate (~1.5 nm s⁻¹), hence the etching is done in 10s increments to prevent overheating of the photoresist mask. A second silicon nitride layer with the thickness of 100nm is deposited to encapsulate the microheaters (figure 1(f)). After etching a window in the top LSN layer, the metal contacts are defined through photolithography, evaporation of 90nm Pt on a 10nm Ti adhesion layer and lift-off in acetone (figure 1(g)). Finally, a window is plasma-etched on the back-side of the wafer to expose the silicon substrate, which is etched in a KOH bath (24 wt%) at 80 °C with bubbled oxygen to release the membrane (figure 1(h)). The front-side of the wafer is protected with an alkaline resistant coating (Brewer Science, Protek B3) during the KOH etch. The protective coating is kept in place during the dicing process and removed from individual chips before use.

### 2.2. Microheater testing

The microheater testing is done with a Keithley 2602A source-meter. The current–voltage measurements are taken using LabTracer 2.9 software. The continuous and variable temperature tests are taken with an open-source Java-based program called Zephyr. Modeling conduction with Fourier’s law gives a linear relationship between applied power and the temperature difference between the microheater and room temperature (figure 2(a)). Convection through the air is minimal with the small element size. Radiation modeled based on the Stefan Boltzmann law of blackbody radiation follows \( P = AσεΔT^4 \), which is highly non-linear. However, assuming an emissivity, \( ε \), of 1 and a hot area, \( A \), of 50 × 50 μm, the radiative power barely reaches ~0.1 mW at 700 °C, which is less than 1% of the total applied power. Even considering the radiative loss in the surrounding membrane, assuming a temperature profile that scales logarithmically from the hot area, results in an estimate of radiative power less than 5% of the total applied power. Therefore, in the operating temperature range of the microheater, radiative effects can be considered to be negligible. Given the linear relationship between applied power and temperature, the temperature can be defined with two calibration points. The first is at room temperature and the second is done by powering the heater to the glowing point and then fitting the emission spectrum with a Planck distribution [26, 29]. The emitted spectrum over a range of wavelengths is collected using a spectrometer.
with a small spot area focused on the hottest area. The onset of visible glow is found to be ~700 °C which is 21 mW for the polysilicon microheaters and 28 mW for the SiC heaters. Although measuring the heater resistance during external heating is a common temperature calibration technique, it is not accurate for this microheater platform because the colder parts of the heater contribute a non-negligible portion of the total resistance. Therefore, external heating where the entire chip is at a given temperature does not provide the same resistance as when only the hot zone of the microheater is at that temperature.

2.3. Sensor fabrication and testing

The platinum nanoparticle-loaded boron nitride aerogel (Pt-BN) synthesis and characterization can be found in full detail in [25]. Scanning electron microscopy imaging is done with a Zeiss LEO 1550 system to observe the aerogel morphology. For sensor testing, a microheater chip is wire-bonded into a ceramic dual in-line package (figure 2(b)). The Pt-BN is suspended in isopropyl alcohol (IPA) with sonication and a few microliters are dropped onto the chip while the microheater is heated to the boiling point of IPA (80 °C) to facilitate local deposition. The packaged sensor is exposed to the gases of interest in a 1 cm³ Teflon chamber. Propane (5% in N₂, Praxair), oxygen, and nitrogen gas flow rates are set by a Labview program that controls Bronkhorst mass flow controllers. The oxygen concentration is kept constant at 20% with nitrogen as the balance and the total gas flow rate is set to 300 sccm. A Keithley 2602A source-meter and Zephyr software are used to apply a given potential to the sensor and record the sensor resistance in response. Sensing response is reported as \( \frac{R_{\text{gas}} - R_0}{R_0} \times 100\% \) where \( R_{\text{gas}} \) is the sensor resistance during exposure to a given concentration of gas and \( R_0 \) is the sensor resistance in synthetic air only.

3. Results and discussion

3.1. Microheater characterization

The current–voltage sweeps of the SiC and polysilicon microheaters are shown in figures 3(a) and (b). The resistance versus power relationship is calculated from the current–voltage sweep and plotted in figures 3(c) and (d). Because the power is linearly proportional to the heater temperature in the range up to 700 °C, the resistance-power relationship is functionally the same as the resistance-temperature relationship. The SiC microheaters have a higher resistance at room temperature, about 60 kΩ compared to 1.25 kΩ for the polysilicon microheaters. The SiC microheaters require a higher applied voltage...
TCR values are increasing with temperature and the SiC resistance decreasing opposite in sign and non-linear, with the polysilicon resistance temperature. To reach 500 °C, the polysilicon microheater requires 15 mW while the SiC microheater requires 20 mW, which is attributable to the higher thermal conductivity of SiC compared to polysilicon [13]. With a higher thermal conductivity, the silicon carbide trace can sink more heat into the substrate, lowering the heating efficiency and increasing the power required to reach a given temperature.

As is evident from figures 3(c) and (d), the two microheaters have temperature coefficients of resistance that are opposite in sign and non-linear, with the polysilicon resistance increasing with temperature and the SiC resistance decreasing with temperature. With the heater at 500 °C, the calculated TCR values are +350 ppm K⁻¹ for polysilicon and −700 ppm K⁻¹ for polySiC. The magnitude and sign of the SiC TCR are comparable to prior reports [21, 30]. The sign of the microheater TCR is controlled by the competing effects of increased phonon scattering in the crystal grain leading to an increasing resistance with temperature, and thermal activation of carriers across the grain interfaces leading to a decreasing resistance with temperature. The change in slope observed in polysilicon at 14 mW coincides with the recrystallization temperature. Because the magnitude of the SiC TCR is twice as large as the polysilicon, the same change in temperature due to gas combustion results in a larger resistance change from SiC than from polysilicon, making it a more sensitive transducer for catalytic gas sensing.

When both microheaters are continuously powered at 500 °C for 100h (figure 4), the SiC microheater shows an order of magnitude lower drift (−0.6%) than the polysilicon (7%). The resistance of each microheater is normalized to the initial value for easier comparison. The SiC microheater displays a higher noise level, possibly due to the lower current level used to reach the operating temperature. Previous reports have also shown long-term positive resistance drift in polysilicon microstructures at temperatures close to 500 °C [9, 11], and suggest the cause may be dopant segregation at grain boundaries or dopant diffusion along the temperature gradient. Some decrease in the rate of drift is observed over the first 100h, suggesting that with a longer ‘burn-in’ or conditioning time, the drift could be mitigated. However, during catalytic gas sensing, the combustion of the target gas leads to an increase in temperature above the 500 °C heater baseline; thus the microheater behavior must be stable with changing high temperature as well as with a constant baseline.

To demonstrate this issue, applying a set of temperatures from 510 to 650 °C with a baseline of 500 °C (figure 5(a)) results in major instability in the polysilicon microheater, including history dependence (figure 5(b)) where the response depends on what temperatures are previously reached. The recrystallization temperature of polysilicon is around 600 °C [9]; thus the resistance decrease when the microheater is held at the highest temperature may be due to grain growth. During the return to baseline, the resistance increases again just as with the long-term drift observed in figure 4. In a previous report, the resistance of a polysilicon heater at low temperature depends on the high temperature previously reached and the cooling rate [9]. In the temperature profile applied in figure 5(a), the temperature switching is done in the same length of time but with different temperature changes, so the cooling rate differs for each temperature reached. This may explain why the polysilicon microheater returns to different resistance values after reaching various elevated temperatures. In contrast to this unpredictable behavior, the SiC microheater displays stable baseline recovery even when heated to 650 °C (figure 5(c)) as well as stable resistance values when the temperature is held constant at a particular value. The high chemical stability and wide bandgap of silicon carbide microheater make it highly resistant to thermally induced resistance drift, which makes it the superior choice for a sensing platform with high operating temperature.

3.2. Catalytic gas sensing response

With the addition of Pt-BN as the catalytic material (figure 6(a)), the SiC platform can be used for catalytic gas sensing. Figure 6(a) shows the Pt-BN after drop-casting on top of the silicon carbide microheater. As a commonly used fuel, refrigerant, and process chemical, propane is used to demonstrate the sensor performance [31, 32]. Although the auto-ignition temperature for propane is 450 °C, there is no response from the bare microheater. Other researchers have shown that small
microheater-based sensors are inherently explosion-proof without expensive packaging [33]. The lower explosive limit (LEL), defined as the lowest concentration capable of producing an explosion, for propane is 2.1% or 21,000 ppm; thus, the sensor is exposed to concentrations below that value. As shown in previous work [25], the sensors made with bare boron nitride aerogel do not show any propane response, indicating the platinum nanoparticles are required for gas combustion.

The SEM image of the Pt-BN in figure 6(b) shows the high surface area morphology of the material. The transmission electron microscopy analysis reported previously indicates that the average Pt nanoparticle diameter is 17 nm and the platinum is crystalline and well-adhered to the boron nitride aerogel [25]. Earlier analysis also shows that the boron nitride aerogel scaffold is 7–10 layers thick and the specific surface area is calculated to be 450 m² g⁻¹ before platinum loading using nitrogen adsorption [25]. The high specific surface area allows for high nanoparticle loading with minimal support mass, improving the transfer efficiency of the heat generated during hydrocarbon combustion and the response time. The boron nitride aerogel scaffold is chosen because of the improved thermal stability it gives over graphene aerogel.

Figure 7(a) shows the effect of temperature on sensor response to 2% propane, where the response is defined as the percentage change in resistance. The figure shows that above 300 °C, the propane response monotonically increases with

Figure 5. (a) Temperature profile applied to the microheaters and resulting (b) polysilicon and (c) polySiC microheater resistance.

Figure 6. (a) Optical image of the Pt-BN catalyst after drop-casting on top of the microheater. (b) SEM image of the Pt-BN showing the high surface area morphology.
temperature. Even at 500 °C, the sensor has not reached a mass-transfer limited regime, beyond which point the sensitivity is expected to not change as strongly with temperature. Operating in a kinetically-limited regime impacts the linearity of the response with concentration, because as the sensor responds and heats up, the rate of reaction increases, leading to further increase in the temperature and rate. This explains the nonlinearity seen in the response versus concentration curve in figure 7(b). Operating at higher temperatures in order to reach a mass-transfer limited regime is possible with the silicon carbide microheater, but the power consumption increases. Also, as temperature increases above 700 °C, the relationship between power and temperature starts to become non-linear as radiative heat loss becomes more significant, making it much more difficult to interpret the signal.

The Pt-BN SiC sensor resistance shown in figure 7(c) with varied propane gas exposure shows a high degree of stability in the baseline and reproducibility in response. In between the propane exposures, clean, dry synthetic air is flown over the sensor. Exposure to 20000 ppm propane results in an approximately 65 °C increase of the microheater temperature, as estimated from the resistance versus temperature calibration curve, but the sensor recovers well to the baseline after gas exposure. Using a signal-to-noise ratio of 3, the limit of figure 8. Pt-BN SiC sensor response to 2% propane over 36 h of operation compared to Pt-BN, Pt-GA, and a Pt thin film on the polysilicon microheater.
likely that the instability in the polysilicon microheater is caused by the catalytic material but shows no change in response over 36 h. The Pt-BN SiC sensor uses the same catalytic material as the Pt-GA graphene aerogel (Pt-GA) on a polysilicon microheater. The Pt-BN SiC sensor maintains good propane response in a propane sensor with improved response stability. As seen in figure 8, the Pt-BN SiC sensor response is highly stable over a 36 h period of extended continuous operation at 500 °C where the sensor is alternately exposed to clean air and various concentrations of propane. Figure 8 only shows the response to 2% propane for clarity, even though the sensor is exposed to varied concentrations during this test. The response stability is also compared to that of the Pt-BN on a polysilicon microheater and platinum nanoparticle-loaded graphene aerogel (Pt-GA) on a polysilicon microheater. The graphene aerogel has been shown to burn off of the microheater during testing [24, 26].

Functionally, this suggests that for accurate propane detection, the catalytic gas sensor must be paired with an oxygen sensor. However, for a simple alarm for leak detection, an increased propane concentration displaces some of the oxygen, giving a larger sensor response as the leak worsens.

In addition to propane, the Pt-BN SiC sensor also responds to hydrogen gas (figure 9(c)). The sensitivity for hydrogen is larger than for propane even though the combustion energy per mole of gas is lower for hydrogen. This is probably due to the faster reaction kinetics. For some catalytic gas sensing applications, this lack of selectivity may be allowable, as the sensor warns of any potential combustible gas. To improve the selectivity, it is possible to measure the sensor response at various operating temperatures and using analysis such as principal component analysis, determine the contribution of...
each gas in the mixture to the total response [36–38]. Each gas has a unique response curve with temperature; for example, hydrogen gas has a high response starting at temperatures of 300 °C [26]. The fast thermal response of the microheater can allow for rapid scanning through various operating temperatures. Further improvements in catalyst design may also allow for more selective measurements.

4. Conclusion

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

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