

Thermal Detection Mechanism of SiC-Based Resistive Gas Sensors

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ABSTRACT

Silicon carbide-based resistive gas sensors from our laboratory have been previously reported to detect hydrogen at concentrations ranging from less than 1% to 100% H₂ in Ar and at temperatures ranging from 50°C to 450°C. The gas sensing mechanism for these devices was not well understood, hindering further improvement in this technology. In this report, resistive devices built on a thin 3C-SiC epitaxial layer grown on 150Å thick Si layer wafer bonded to a polycrystalline SiC substrate were studied. The polycrystalline SiC substrate is insulating, allowing the formation of isolated epitaxy resistors on the 3C-SiC layer. The gas sensing devices consisted of rectangular ohmic NiCr contacts with a Au overlayer fabricated on the 3C-SiC surface. Under a constant dc bias, nominally 10V in this study, these sensors demonstrated a decrease in current of up to ~25.4 mA upon the introduction of 100% H₂, relative to 100% N₂ in the test gas stream. The time constant for this device, estimated as a first-order exponential decay, was ~16-22 sec, with the full response occurring after ~90-120 sec. Upon the introduction of 100% H₂ to the sensing environment, the device temperature, as measured by an resistance temperature detector (RTD) in intimate thermal contact with the device, decreased from 400°C to 237°C ($\Delta T = \sim 163^\circ\text{C}$). This large decrease in device temperature was driven by increased heat transfer coefficient of H₂ relative to N₂. The sensitivity to CH₄ in N₂, CO₂ in N₂ and He in Ar was also tested. Sensitivities, defined as the smallest change in concentration, as low as 300 ppm H₂ in N₂ were achieved with devices operating at 400°C and 10 V dc. Details of the device performance and a model of the sensing mechanism will be discussed.

INTRODUCTION

High temperature extreme environment gas sensing is of great interest to the automotive [1,2], aerospace [3] and chemical industries [4] for safety and process control. For operation at high temperatures (> 200°C), wide-bandgap materials such as silicon carbide (SiC) are generally required [5]. Several device structures, including Schottky-barrier diodes and metal-oxide-semiconductor field-effect transistors (MOSFETs), have been employed to detect a wide range of gases. Schottky-barrier diode and MOSFET sensors are used in conjunction with a catalytic gate, such as Pt, Pd, Ru, or Ir, to aid in the detection of hydrogen-containing species. The detection mechanism of these devices is known to be driven by the dissociation of H containing species on the catalytic metal surface and the diffusion of atomic H to the metal-insulator interface, creating a dipole

layer that changes the electrical properties of the device [6]. Recently, resistive SiC gas sensors have been reported to detect H₂ at concentrations ranging from 0.33% to 100% H₂ in Ar at temperatures ranging from 50°C to 400°C [7,8]. The detection mechanism driving these resistive gas sensors is not fully understood, and is the focus of this study.

EXPERIMENTAL

In this study, a thin 3C-SiC film was deposited on a thin Si (001) layer (~ 150 Å), miscut 4° towards the [211] direction, bonded to a polycrystalline SiC substrate using a wafer bonding process described elsewhere [9]. The 3C-SiC deposition was carried out in a low-pressure, hot-wall, horizontal chemical vapor deposition (CVD) reactor using the traditional dual precursor gas chemistry, propane (C₃H₈) and silane (SiH₄), with hydrogen chloride (HCl) used as a growth promoter [10]. The 3C-SiC epitaxial layer was grown at 1360°C and 200 Torr with Si/C and Si/Cl ratios fixed at 0.7 and 3.3, respectively. The 3C-SiC film was determined to be ~ 1.4 μm thick measured via FTIR.

After growth of the 3C-SiC epitaxial layer, 5000 Å of SiO₂ was deposited on the 3C-SiC surface by plasma enhanced CVD (PECVD) using SiH₄ and NO₂ precursors. Windows were etched in the SiO₂ layer to define the active sensor area after which NiCr (~2000 Å) contacts were deposited by electron-beam evaporation. These contacts were then rapid thermally annealed at 950°C for 2 minutes in an Ar ambient to produce ohmic contacts. A Ti (200 Å)/Au (4000 Å) stack was then sputtered on the annealed NiCr to allow for Au wire bonding. A schematic of the device is shown in Figure 1a. After fabrication, devices were mounted on a Pt-100 resistive temperature detector (RTD) and placed on a ceramic heater. The device contacts were then wire bonded to a 16-pin Au package, shown in Figure 1b.

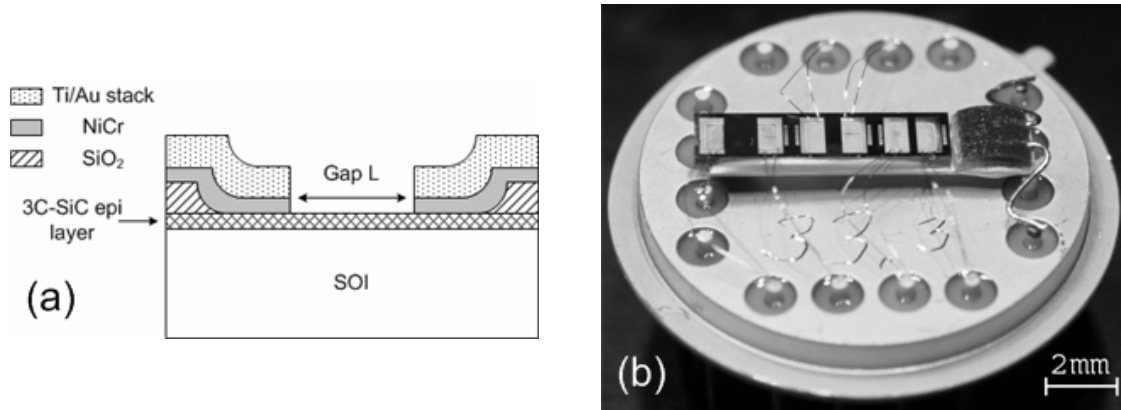


Figure 1. (a) Cross sectional diagram of 3C-SiC/SOI resistive gas sensor and (b) photograph of packaged sensor.

The packaged sensors were placed in an aluminum plenum housing with each sensor compartment measuring approximately 25.4 mm x 25.4 mm x 9.5 mm with ~ 4 mm of space for gas to flow over each sensor. The Al housing was connected to a gas manifold system and the gas sensors were tested in various H₂/N₂, CO₂/N₂, CH₄/N₂, and He/Ar atmospheres.. The composition and flow rates of the gases (maintained at a total flow of 100 sccm for all experiments) were digitally controlled via computer-operated

mass flow controllers. The resistive gas sensors were tested under a constant dc bias while the current flowing through the sensors was measured by the voltage drop across a precision resistor [11], with a value of either $1 \pm 0.02\%$ or $100 \pm 0.005\%$ Ω , allowing real-time measurement of the sensor resistance via Ohm's law.

RESULTS AND DISCUSSION

Figure 2 shows the current flowing through a 3C-SiC/SOI resistive gas sensor, with 0.5 mm x 0.25 mm contacts and 0.25 mm gap, in response to 10% to 100% H₂ in N₂ at 400°C while under 10 V dc bias. The average current at steady-state in this device decreased from a "baseline," when exposed to 0% H₂ (100% N₂), of 48.9 ± 0.2 mA to 23.49 ± 0.02 mA when exposed to 100% H₂, corresponding to a $51.75 \pm 0.04\%$ decrease in current. The time constant for this device, estimated as a first-order exponential decay, was ~16-22 sec, with the full response occurring at ~90-120 sec after the initial introduction of the gas mixture and is strongly dependent on the H₂ concentration. These response times are a drastic improvement from our previous reports where 420-900 second response times were observed [7,8]. This decrease in response time is attributed to the smaller volume of gas surrounding the sensor compared to our previous work (~6 cm³ versus ~20 cm³), giving an increased gas velocity at a constant volumetric-flow rate of 100 sccm. With this 3C-SiC/SOI sensor operating at 400°C and with a 10 V dc bias, the measurement error in resistance is between 0.3 and 4.2 Ω . With this measurement error defining the sensitivity of these sensors, the smallest change in H₂ concentration that can be measured is between ~300 ppm and ~2000 ppm (or 0.2 %).

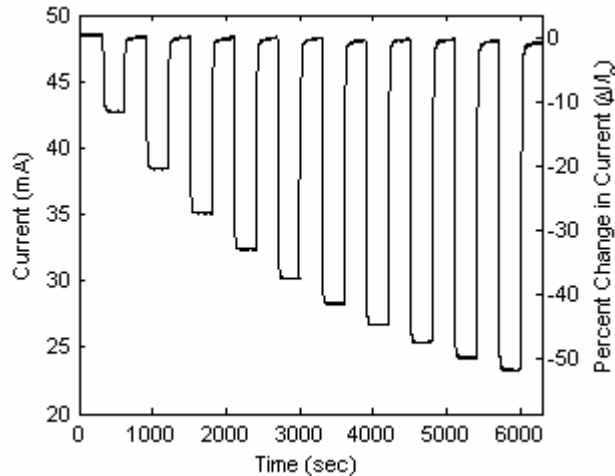


Figure 2. Measured current (left axis) and percent change in current (right axis) of a 3C-SiC/SOI resistive gas sensor, with 0.5 mm x 0.25 mm contacts and 0.25 mm gap, in response to 10% to 100% H₂ in N₂ in 10% increments at an initial device temperature of 400°C.

Initial reports attributed the changes in current upon the introduction of H₂ to the gas stream over the sensor device demonstrated in Figure 1 to the adsorption of H₂ on the

sensor surface and its influence on the resistance of the sensor. However recent evidence has indicated a thermal detection mechanism. Figure 3 shows the temperature of the same device, as measured by the RTD on the sensor package, while detecting the same H₂ pulses depicted in Figure 2. Figure 3 clearly shows the device temperature decreasing when exposed to H₂ with a temperature decrease of up to $163.1 \pm 0.4^\circ\text{C}$ when pure H₂ was introduced. It is well known that the resistivity of a semiconductor is strongly temperature dependent [12]. Thus, the large temperature decreases shown in Figure 3 will cause the device resistivity, or resistance, to change. These changes in resistance are measured as changes in current flowing through a device at a fixed voltage, as shown in Figure 2.

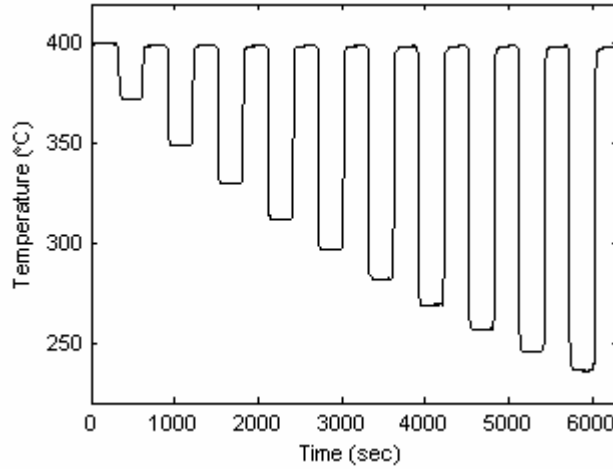


Figure 3. Measured temperature of a 3C-SiC/SOI resistive gas sensor, with 0.5 mm x 0.25 mm contacts and 0.25 mm gap, in response to 10% to 100% H₂ in N₂ in 10% increments at an initial device temperature of 400°C.

The temperature changes depicted in Figure 3 are caused by different amounts of heat, generated by Joule heating of the device and ceramic heater, transferred from the device to the gas. This heat transfer can be described by a differential energy balance for a differential unit volume of the device, shown in equation (1) [13]:

$$\frac{\partial}{\partial t}(\rho C_p T) = \sigma |\nabla V|^2 + k \nabla^2 T \quad (1)$$

where ρ is the density, C_p is the specific heat, σ is the electrical conductivity, k is the thermal conductivity of the device, and V and T are voltage and temperature, respectively. The boundary conditions for this partial differential equation are 1) $T = T_o$ for $t = 0$ at all boundaries and 2) $q = q_{heater}$ for $t > 0$ at the device/heater interface, where q is heat flux. Newton's law of cooling defines the heat flux for $t > 0$ and for all boundaries except the device/heater interface is shown in equation (2) [13].

$$q_{surface} = h(T_{gas} - T_{surface}) \quad (2)$$

The energy balance in equation (1) only accounts for the transport of energy in the device. It is the boundary condition in equation (2) that describes the interaction between the gas and the device. The inlet gas temperature (T_{gas}) is approximately room temperature (25°C) and is relatively constant ($\pm 2^\circ\text{C}$) throughout these experiments. Thus, the amount of heat transferred to the gas ($q_{surface}$) is related to the temperature of the surface ($T_{surface}$) only through the heat transfer coefficient (h). It is the heat transfer coefficient that changes with the composition of the gas through the specific heat (C_p), thermal conductivity (k), and viscosity (μ) of the gas mixture [14] that is responsible for the sensing of gases through a thermal detection mechanism.

The sensitivity of these 3C-SiC/SOI resistive gas sensors to other gases was also tested. Figure 4 shows the current flowing through a 3C-SiC/SOI resistive sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap operating at an initial temperature of 100°C and a 10 V dc bias, in response to high concentrations (10% to 100%) of H₂, CH₄, and CO₂ in N₂ and He in Ar. For the H₂, CH₄, and He test gases, the current decreased with increasing gas concentration due to decreases in the device temperature while the current increased when CO₂ was tested. The temperature changes caused by the introduction of different gases are due to differing amounts of heat transferred to the gas, through differing heat transfer coefficients relative to the purge gas. The sensor responses shown in Figure 4 demonstrate the ability of 3C-SiC/SOI resistive sensors to detect a wide range of gases in several ambients through a thermal detection mechanism.

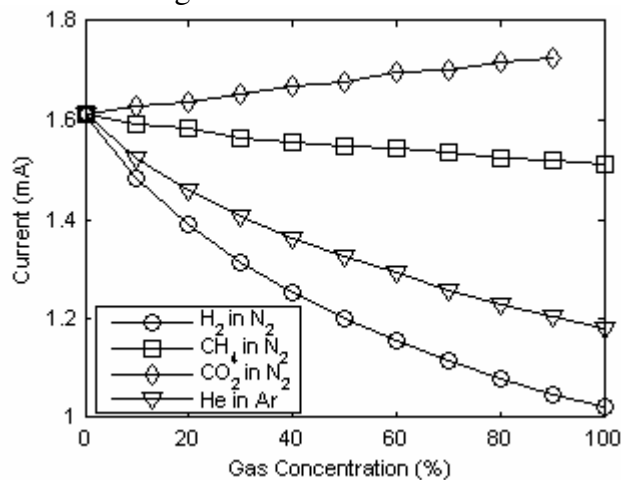


Figure 4. Measured current flowing through a 3C-SiC/SOI resistive gas sensor, with 0.5 mm x 1 mm contacts with a 1 mm gap, in response to (10% to 100% of several gases in either N₂ or Ar at an initial device temperature of 100°C and a bias of 10 V DC

CONCLUSIONS

3C-SiC/SOI resistive gas sensors were fabricated and shown to be sensitive to H₂ in N₂, CH₄ in N₂, CO₂ in N₂, and He in Ar at concentrations ranging from 10% to 100% and at temperatures ranging from 100°C to 400°C. Our initial reports suggested a surface adsorption mechanism for gas detection [7,8]. However recent device temperature

measurements strongly support a thermal detection mechanism with large temperature changes, up to $\sim 163^{\circ}\text{C}$, observed upon the introduction of pure H_2 , relative to pure N_2 . This thermal detection mechanism is driven by the transfer of heat from the device to the gas with differences in the heat transfer coefficients of gases changing the temperature of the device. Since the resistivity of semiconductor materials is highly temperature dependent, even small changes in temperature can be readily observed as changes in resistivity. These resistivity changes can be measure electronically using a resistive device structure and correlated to the concentration of the target gas(es) via the proposed thermal detection mechanism for the 3C-SiC/SOI resistive sensor presented in this study.

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