Thermal detection mechanism of SiC based hydrogen resistive gas sensors

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(Received 11 April 2006; accepted 24 August 2006; published online 30 October 2006)

Silicon carbide (SiC) resistive hydrogen gas sensors have been fabricated and tested. Planar NiCr contacts were deposited on a thin 3*C*-SiC epitaxial film grown on thin Si wafers bonded to polycrystalline SiC substrates. At 673 K, up to a 51.75±0.04% change in sensor output current and a change in the device temperature of up to 163.1±0.4 K were demonstrated in response to 100% H_2 in N_2. Changes in device temperature are shown to be driven by the transfer of heat from the device to the gas, giving rise to a thermal detection mechanism. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2360905]

Gas sensors that can operate at high temperatures and in harsh environments are needed for fuel cell,[1] aerospace,[2] and automotive[3] applications. These applications often require sensor operation at temperatures in excess of 923 K and involve corrosive chemical species such as NO_x.[2,3] Wide band gap semiconductor materials with excellent chemical and thermal stabilities, such as silicon carbide (SiC), are being investigated for use in harsh high temperature environments.[3–5] This wide band gap [2.36 eV for 3*C*-SiC (Ref. 6)] allows these materials to operate at elevated temperatures in comparison to silicon (1.1 eV).[7]

Devices based on SiC for gas sensing have included Schottky barrier diodes[2,4] and metal-oxide-semiconductor field-effect transistors (MOSFETs),[3,5,8] each of which employ a catalytic metal gate to drive their detection mechanisms. Recently, resistive device structures have been investigated for their potential use as gas sensing devices.[9,10] Resistive gas sensors possess several advantages over other sensor device structures including a simplified device fabrication and no catalytic gate metal that can be poisoned during operation.[8] Also, resistive sensors have demonstrated the ability to detect a wide range of H_2 concentration, from 0.33% to 100% H_2 in Ar,[9,10] a range not seen in catalytic gate Schottky diode or MOSFET sensors.[1,3–5]

Resistive gas sensors were fabricated from a thin 3*C*-SiC film grown on a 15 nm thick Si layer, which was bonded to a polycrystalline SiC substrate, referred to as silicon on insulator (SOI) in this letter, by a wafer bonding process that is described elsewhere.[11] In this work, a hot-wall SiC chemical vapor deposition (CVD) reactor operating at low pressure was used to grow the 3*C*-SiC film on the SOI substrate. Details of the 3*C*-SiC growth process are described elsewhere.[12] The 3*C*-SiC epitaxial film was measured to have a thickness of 1.4 μm, as determined by Fourier transform infrared spectroscopy measurements.

After CVD growth a 5000 Å thick SiO_2 layer was deposited on the 3*C*-SiC surface via plasma enhanced chemical vapor deposition. The sensor active areas were then etched in the SiO_2 layer, followed by the deposition of NiCr (~2000 Å) contacts via e⁻-beam evaporation. These contacts were then rapid thermally annealed for 120 s at 1223 K in an Ar ambient to produce contacts with Ohmic-like behavior. A Ti (200 Å)/Au (4000 Å) stack was then sputtered on the annealed NiCr to allow for Au wire bonding. Several devices were fabricated on the same die, with contact dimensions of either 0.5×0.25 mm^2 or 0.5×2 mm^2 and a gap of 0.25 mm between the contacts. A schematic of the device structure and characteristic linear current versus voltage characteristics are shown in Fig. 1.

Devices were then mounted together with a Pt-100 resistance temperature detector (RTD) and placed on a ceramic resistive heater. The contacts were then wire bonded to a 16-pin gold package described elsewhere.[3] The packaged sensors were placed in an aluminum plenum housing that was connected to a gas manifold system and the gas sensors were tested in various H_2/N_2 atmospheres. The composition and flow rates of the gases [maintained at a total flow of 100 SCCM (SCCM denotes cubic centimeter per minute at STP) for all experiments] were digitally controlled via

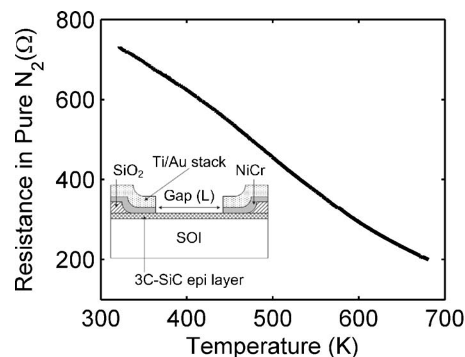

FIG. 1. Calculated resistance as a function of measured temperature for a 3*C*-SiC/SOI sensor, with 0.5×0.25 mm^2 contacts and 0.25 mm gap, while exposed to 100% N_2. The inset shows cross section of 3*C*-SiC/SOI resistive sensor structure.

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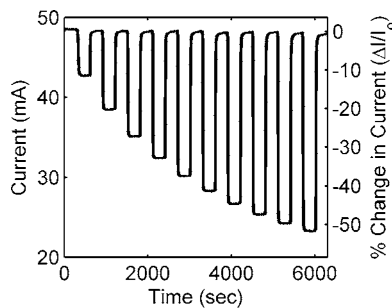

FIG. 2. Measured current (left axis) and percent change in current (right axis) flowing through a 3*C*-SiC/SOI resistive gas sensor, with $0.5\times0.25\ \mathrm{mm}^2$ contacts and 0.25 mm gap, in response to 10%–100% H_2 in N_2 in 10% increments at an initial device temperature of 673 K.

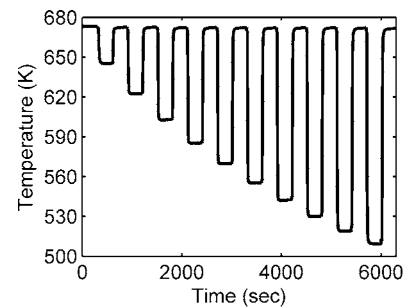

FIG. 3. Measured temperature of a 3*C*-SiC/SOI resistive gas sensor, with $0.5\times0.25\ \mathrm{mm}^2$ contacts and 0.25 mm gap, in response to 10%–100% H_2 in N_2 in 10% increments at an initial device temperature of 673 K.

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, rated at $1\pm0.02\%\ \Omega$, allowing real-time measurement of the sensor resistance via Ohm's law. For all experiments, the voltage of the heater was set such that the desired temperature was obtained in pure N_2 and held constant throughout the duration of each experiment.

Figure 2 shows the current flowing through a resistive gas sensor, with $0.5\times0.25\ \mathrm{mm}^2$ contacts and 0.25 mm gap, in response to H_2 exposure from 10% to 100% in a N_2 ambient. The H_2 concentration was varied in 10% increments at an initial device temperature of 673 K while under a constant 10 V dc bias. In this device, the current decreased as H_2 was added to the N_2 ambient with a decrease of up to $51.75\pm0.04\%$, when pure H_2 was introduced to the gas sensor as calculated from the steady-state portion of the response from the "base line" value. The base line is defined as the sensor response to 0% H_2 (i.e., 100% N_2 ambient). The time constant for this device, estimated as a first order exponential decay, was ~16–22 s, with the full response occurring at ~90–120 s after the initial introduction of the gas mixture and is strongly dependent on the H_2 concentration. This response time is a dramatic improvement from our previous reports, where 420–900 s to full response was not uncommon,[9,10] which is likely a result of the decreased volume of the measurement chamber. This device demonstrated measurable changes in current of ~1 mA at H_2 concentrations in a N_2 ambient as low as 1% at 673 K.

In a previous letter,[9] we discussed the possibility of the resistive gas sensor response being driven by the adsorption of H_2 on the 3*C*-SiC surface. However, new evidence has pointed to thermal effects driving the gas detection. Figure 3 shows the temperature of the same device, as measured via the resistance of the aforementioned RTD in intimate thermal contact with the sensor, while detecting the H_2 pulses whose responses are shown in Fig. 2. It is clearly seen in Fig. 3 that the temperature of the device decreases when the sensor is exposed to H_2, with a temperature decrease of up to 163.1 ± 0.4 K when pure H_2 was introduced. It is well known that the resistivity of a semiconductor is strongly temperature dependent.[13] Thus, the temperature decrease, shown in Fig. 3, causes a change in the resistivity of the semiconductor material, as seen in the decreasing current shown in Fig. 2.

The temperature of the device is governed by the amount of heat transferred from the device to the gas. The heat generated by Joule heating of the resistive gas sensor is transferred to the gas with a magnitude dependent on the thermal properties of gas through Newton's law of cooling ($q_{\mathrm{surface}}=h(T_{\mathrm{gas}}-T_{\mathrm{surface}})$).[14] The inlet gas temperature (T_{gas}) is approximately room temperature (300 K) and is relatively constant (±2 K) throughout these experiments. Thus, the amount of heat transferred to the gas (q_{surface}) is related to the temperature of the surface (T_{surface}) only through the heat transfer coefficient (h). It is the heat transfer coefficient that changes with the composition of the gas through the specific heat (C_p), thermal conductivity (k), and viscosity (μ) of the gas mixture[14] that is responsible for the sensing of gases through a thermal detection mechanism.

The transfer of heat from the device to the gas will occur regardless of which gas and/or gas mixture is flowing over the sensor. However, the magnitude of heat transfer will clearly depend on the thermal properties of the gas. Thus, these sensors actually detect thermal changes relative to a reference gas, which is N_2 for these experiments. A decrease in temperature upon the introduction of H_2, as exhibited in Fig. 3, suggests that H_2 removes more heat from the sensor than N_2, a fact that is well known,[15] and supported by the thermal properties of H_2 ($k=0.291$ W/m K, $C_p=29.73$ J/mol K) relative to N_2 ($k=0.0441$ W/mol K, $C_p=29.75$ J/mol K) at 600 K.[16]

Figure 4 shows the mean resistance (as calculated from the measured instantaneous sensor voltage and current) of a resistive gas sensor, with $0.5\times2\ \mathrm{mm}^2$ contacts and 0.25 mm gap, as a function of H_2 concentration at 673 K for several gas sensor voltages (2.5, 5, and 10 V). Increasing gas sensor voltage increases the Joule heating effects such that more heat is transferred to the gas. With more heat transferred to the gas, the more the device surface temperature (T_{surface}) will decrease, also shown in Fig. 3, with a constant heat

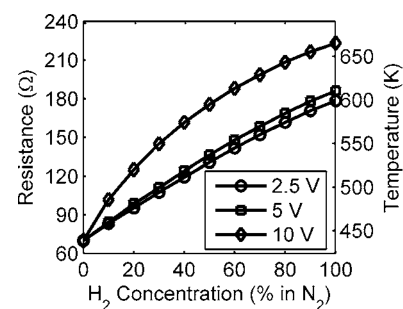

FIG. 4. Calculated resistance (left axis) and measured temperature (right axis) vs H_2 concentration (N_2 ambient) for a 3*C*-SiC/SOI sensor, with $0.5\times2\ \mathrm{mm}^2$ contacts and 0.25 mm gap, at an initial device temperature of 673 K for bias voltages of 2.5, 5, and 10 V dc.

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transfer coefficient as governed by Newton's law of cooling. This increased change in temperature results in an increased change in resistance, as demonstrated in Fig. 4. Thus, the higher the Joule heating, the higher the gas sensor response.

These 3*C*-SiC resistive gas sensors can be compared to thermistor devices, made primarily from metal oxides such as $BaTiO_3$ (Ref. 17) and $SrTiO_3$,[18] whose highly temperature dependent resistance is used as a temperature transducer for a variety of applications. Thermistor devices have also been used to indirectly measure heat transfer coefficients for convective heat transfer,[19] similar to those used in the measurements presented in this letter. Thermal conductivity sensors fabricated from materials such as Pt (Ref. 20) and poly-Si (Ref. 21) have also been used to measure the thermal conductivity of gas mixtures and for gas detection.

In summary, a 3*C*-SiC/SOI resistive sensor has been fabricated and shown to be capable of detecting H_2 over a wide range of concentrations from 10% to 100% H_2 in N_2 and at a relatively high temperature of 673 K. Initial investigations proposed the dissociation of H_2 on the exposed SiC surface, giving rise to a change in surface conductivity, as the gas sensing mechanism.[9,10] In contrast to this surface conductivity proposition, this letter provides evidence that the gas sensing mechanism is most likely driven by thermal effects. With the addition of a temperature sensor to the sensor package, the temperature of the sensor was examined while the sensor was exposed to H_2. A large change in temperature (up to $\sim$163 K) was observed upon the introduction of pure H_2, relative to that in pure N_2. This large change in temperature is driven by the transfer of heat from the device (heat that is provided by both the heater and the Joule heating of the resistive sensor) to the gas. Since the resistivity of semiconductor materials is largely dependent on temperature, even small changes in temperature manifest themselves as a significant change in resistivity. This change can be measured electronically and correlated to the concentration of the target gas(es) via the proposed thermal detection mechanism for the 3*C*-SiC/SOI resistive sensor presented in this study.

This work was supported by the DURINT program administered by the Office of Naval Research (C. Wood) under Grant No. N00014-0110715.

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