Hydrogen Gas Sensors Fabricated on Atomically Flat 4H-SiC Webbed Cantilevers

Philip G. Neudeck1,a, David J. Spry2,b, Andrew J. Trunek2, Laura J. Evans1, Liang-Yu Chen2, Gary W. Hunter1,c, and Drago Androjna3

1NASA Glenn Research Center, 21000 Brookpark Road, M.S. 77-1, Cleveland, OH 44135 USA
2OAI, NASA Glenn, 21000 Brookpark Road, M.S. 77-1, Cleveland, OH 44135 USA
3Sierra Lobo, Inc., NASA Glenn, 21000 Brookpark Rd., M.S. 77-3, Cleveland, OH 44135 USA

aNeudeck@nasa.gov, bDavid.J.Spry@nasa.gov, cGary.W.Hunter@nasa.gov

Keywords: Gas Sensor, Hydrogen, Webbed Cantilevers, Hydrogen Sensor, Atomically Flat, On-axis, Step-free Surface, Schottky Diode, Platinum

Abstract. This paper reports on initial results from the first device tested of a “second generation” Pt-SiC Schottky diode hydrogen gas sensor that: 1) resides on the top of atomically flat 4H-SiC webbed cantilevers, 2) has integrated heater resistor, and 3) is bonded and packaged. With proper selection of heater resistor and sensor diode biases, rapid detection of H2 down to concentrations of 20 ppm was achieved. A stable sensor current gain of 125 ± 11 standard deviation was demonstrated during 250 hours of cyclic test exposures to 0.5% H2 and N2/air.

Introduction

SiC-based gas chemical sensors are under development for use in application environments beyond the operational envelope of other gas sensor approaches [1,2]. However, simultaneous attainment of high sensitivity and stability has proven difficult to achieve for some important harsh application environments. Compared to other harsh-environment micro-sensor approaches, SiC Schottky diode based sensors offer higher sensitivity and signal gains [1,2]. This is because the forward current of the Schottky barrier changes exponentially with small changes in the metal-semiconductor potential barrier height induced by the presence of various gas species. The rise and fall times of sensor currents in response to rapid gas composition changes generally improve as increasing temperature and thinner metallization permit faster transport of gas species to/from the sensitive metal-semiconductor barrier [2]. Previously, we reported “first generation” initial Pt-SiC Schottky contacts deposited on atomically flat SiC epitaxial mesa surfaces (i.e. perfect (0001) basal plane with no atomic-scale steps) that demonstrated greatly improved hydrogen response and stability compared to identical devices on stepped SiC surfaces [1]. This paper reports on initial results from the first device tested of a “second generation” of Pt-SiC Schottky diode hydrogen gas sensor that 1) resides on the top of significantly larger atomically flat 4H-SiC webbed cantilevers [3,4], 2) has an integrated heater resistor, and 3) is bonded and packaged.

Experimental

The basic sensor structure and fabrication process are illustrated in Fig. 1. The first mask patterned an array of pre-growth mesas (Fig. 1, left) by dry-etching to a depth of 30 um into the on-axis 4H-SiC substrate. Thin n-type 4H-SiC lateral cantilevers were then epitaxially grown as reported in [4] to form a relatively large table-like structure with atomically flat (i.e., free of SiC bilayer steps) 4H-SiC top surface. Note that significant growth occurs on the cantilever undersides and mesa sidewalls [4], as shown on the right of Fig. 1. While nominal electrical isolation of the heater resistor from the gas-sensitive Schottky diode might have been achieved by placing the resistor on top of a patterned
A layer of deposited insulator, such an approach would have required at least three additional deposition/patterning steps. Instead, a simplified process was implemented by patterning the same platinum layer (deposited directly onto the step-free n-type 4H-SiC webbed cantilever surface) into both the heating element and gas-sensitive diode. In particular, platinum (2700 Å thick) was sputter-deposited at low power and dry-etch patterned to form both the lateral heater-resistor and the vertical Schottky diode sensing element (Fig. 1, upper right). Following backside metallization, the wafer was diced and then sequentially annealed in air at 150°C for 10 minutes, 300°C for 10 minutes, and 400°C for 30 minutes in an effort to increase device hydrogen sensitivity [1]. One die was then attached to 0.76 mm thick alumina piece in a TO package by conductive epoxy and wire-bonded for initial testing, while others were saved for future high-temperature packaging and testing. The conventionally packaged sensor reported here was tested in a sealed chamber with well-controlled gas flows [5].

Reverse biasing of the heater metal-semiconductor Schottky junction was used to operate the heater resistor with minimal substrate leakage current by grounding one heater terminal and applying negative DC voltage to the other heater terminal with respect to the grounded backside substrate. The sensor Schottky diode was operated at constant positive bias ($V_{Sensor}$) with respect to the grounded n-type SiC (epilayer and substrate) that provided gas-sensitive forward currents in the exponential region of Schottky diode I-V curve that were at least an order of magnitude higher than the reverse-bias heater-to-substrate diode leakage. Electrical measurements reported herein were all conducted using computer-controlled source-measure units. Each measurement was conducted at least 30 minutes after any change in heater bias in order to ensure the device was very close to thermal equilibrium.
Results and Discussion

Fig. 2 summarizes the heater resistor performance characteristics as a function of the magnitude of the applied (negative) heater bias. The average heater filament temperature ($T_H$) shown is estimated from the measured change in the heater resistance ($\Delta R/H$) from the room temperature heater resistance ($R_{H0}$) compared to the previously known $\Delta R/R_0$ values for platinum [6]. The difficult task of thermally modeling this sensor structure (with complicated under-cantilever growth geometry [4]) was not undertaken, so the operating temperature of the Schottky diode sensor element is known only for room temperature (i.e., with no bias applied to the heater). Nevertheless, we suggest that significant under-cantilever SiC deposition combined with the high thermal conductivity SiC adversely affects heater power required to achieve higher temperature operation of this sensor structure.

The forward current-voltage (I-V) characteristics of the sensor element in air (prior to H$_2$ exposure) at four different heater bias currents are shown in Fig. 3a. The exponential portion of the room temperature I-V has a saturation current density $J_0$ of $6.1 \times 10^{-24}$ A/cm$^2$ with an ideality factor $n$ of 1.05. Even for the highest applied heater bias, no reverse Schottky diode leakage current above the measurement noise floor (< 1 nA) was observed. Such low reverse bias leakage indicates that the changes in the sensor’s I-V with heater bias (Fig. 3a) is dominated by thermal coupling instead of electrical coupling between the heater and sensor, as the simplified-process sensor design intended.

Fig. 3b compares the forward I-V’s of sensor in air and 0.5% H$_2$ with the heater biased at $I_H$ of 0 mA and 110 mA. By selecting a proper sensor bias voltage, such as $V_{Sensor} = 1.1$ V for $I_h = 0$ mA or $V_{Sensor} = 0.9$ V for $I_H = 110$ mA, Fig. 3b shows that very large (> 100-fold increases in sensor current) responses to 0.5% H$_2$ are obtained, in spite of the fact that the gold wirebond (Fig. 1) covers about half of the sensor Schottky contact area. Fig. 4a compares the transient responses of the sensor current at these bias conditions to 2 cycles of sequential exposure to air then N$_2$ then 0.5% H$_2$ in N$_2$. Response times are less than a minute. As expected, the heated sensor exhibits somewhat more rapid recovery in air following an H$_2$ exposure. Fig. 4b shows the transient response of the sensor at lower H$_2$ concentrations (20 to 200 ppm in N$_2$) with $I_H = 110$ mA and $V_{Sensor} = 0.9$ V periodically subjected to the 2-cycle gas test profile illustrated in Fig. 4a. The sensor currents measured just prior to the air-to-N$_2$ and H$_2$-to-air gas composition changes for the 2nd cycle (i.e., corresponding to ~28 minutes and ~38 minutes for the $I_H = 110$ mA solid curve in Fig. 4a) are plotted in Fig. 5, along with the resulting H$_2$/Air sensor current gain (i.e., ratio). The measured sensor currents for air and 0.5% H$_2$ remained stable throughout the test duration, resulting in a nearly constant sensor current gain of 125 with standard deviation of ± 11.
Even though the operating temperature is below 150 °C, this gain is more than twice the reported gain of non-atomically flat Pt-SiC Schottky diode hydrogen sensors operating at 200 °C and 300 °C [1].

Summary

Initial testing of the first atomically flat webbed cantilever hydrogen gas sensor device based on simplified single-metal patterning exhibits promising sensitivity and stability characteristics. Further testing of additional devices from the same wafer under broader ranges of operating conditions is necessary and on-going. Based on these initial results, future optimization of webbed cantilever gas sensors appears warranted, and would likely include alternate sensor materials for detection of other gasses (such as hydrocarbons) and revised webbed mesa design to achieve improved thermal isolation and reduced heater power.

Acknowledgement

The authors thank J. Xu, M. Artale, P. Lampard, B. Osborn, M. Mrdenovich, G. Beheim, R. Okojie, J. A. Powell, and L. Matus at NASA Glenn Research Center for their assistance. This work was funded by the NASA Aeronautics Research Mission Directorate in the Fundamental Aeronautics Program, Supersonics Project.

References


Fig. 4. Transient sensor response to cycles of air/N₂/H₂ in N₂ for (a) I_H = 0 (dashed) and I_H = 110 mA (solid) for H₂ concentration of 0.5% in N₂, and (b) for H₂ concentrations down to 20 ppm in N₂ with I_H = 110 mA. Note that the 2nd test cycle in (a) for I_H = 0 (dashed) was initiated 5 minutes later than for I_H = 110 mA (solid).

Even though the operating temperature is below 150 °C, this gain is more than twice the reported gain of non-atomically flat Pt-SiC Schottky diode hydrogen sensors operating at 200 °C and 300 °C [1].

Fig. 5. Sensor currents (I_{Sensor}) and sensor H₂/air current gain measured at V_{Sensor} = 0.9 V with I_H = 110 mA under cyclic exposures to air/N₂/0.5% H₂ in N₂ (see text).