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

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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 H_2 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% H_2 and N_2/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

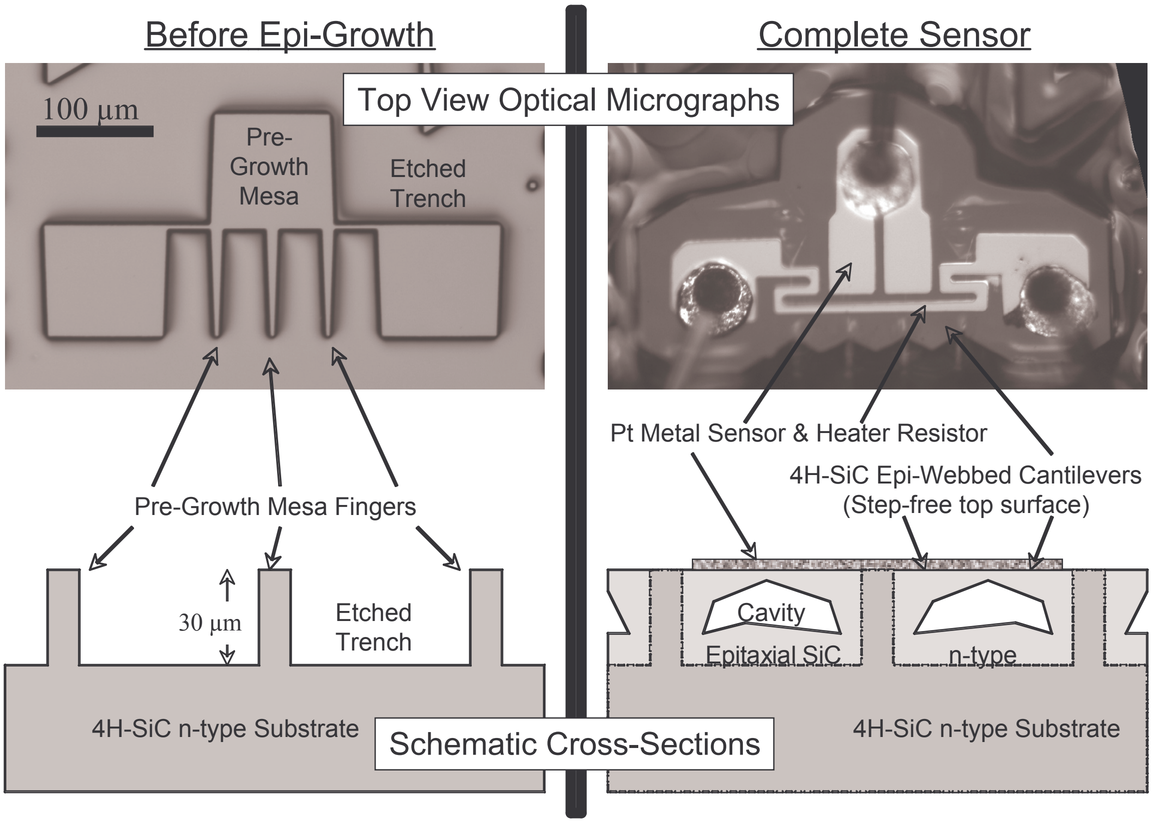

Fig. 1. Top view and cross-sectional illustrations of gas-sensor fabrication. Left side shows pre-epitaxial-growth mesa pattern while right side shows complete sensor with platinum heater resistor and sensor diode residing on top of step-free SiC epitaxial webbed cantilever surface.

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.

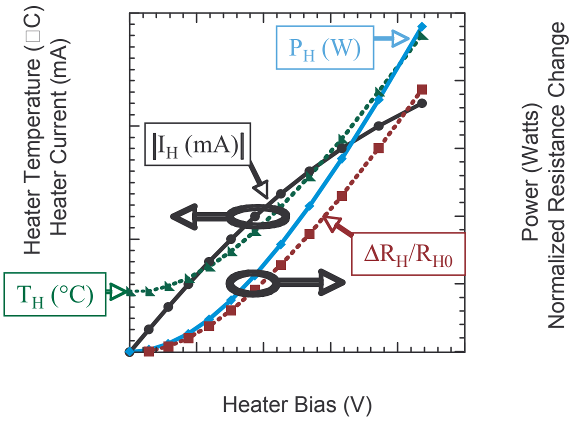

Fig. 2. Heater resistor characteristics as a function of heater bias: current I_H (mA), power P_H (Watts), normalized resistance change from room temperature $\Delta R_H/R_{H0}$, and estimated filament temperature T_H (°C).

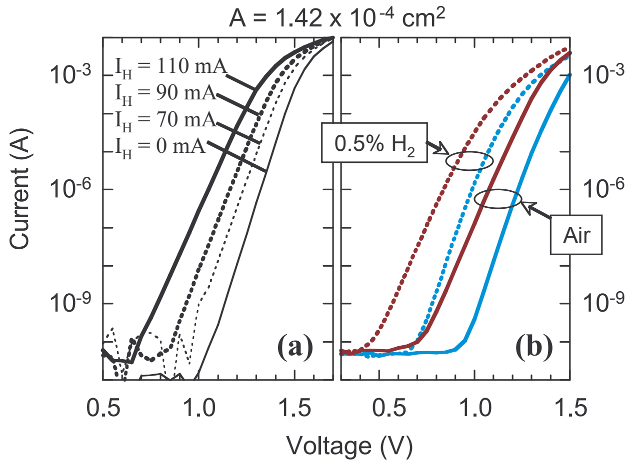

Fig. 3. Sensor Schottky diode forward-bias I-V's (a) for four heater current settings in air prior to intentional H_2 exposure, and (b) in air and 0.5% H_2 at heater current I_H of 0 mA and 110 mA.

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 (ΔR_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 x 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 = 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. The sensor was operated for over 250 hours at 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.

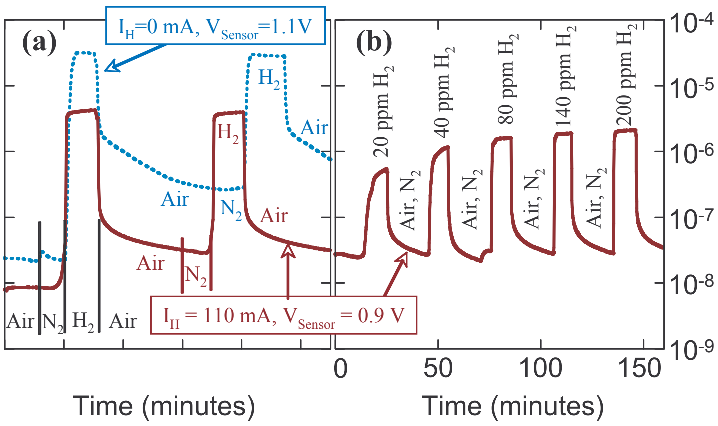

Fig. 4. Transient sensor response to cycles of air/N_2/H_2 in N_2 for (a) I_H = 0 (dashed) and I_H = 110 mA (solid) for H_2 concentration of 0.5% in N_2, and (b) for H_2 concentrations down to 20 ppm in N_2 with I_H = 110 mA. Note that the 2nd test cycle in (a) for I_H = 0 (dashed) was initiated 5 minutes later than for I_H = 110 mA (solid).

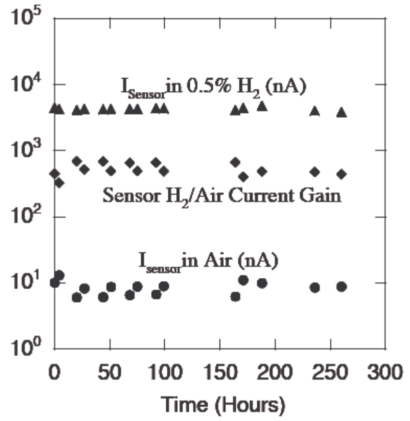

Fig. 5. Sensor currents (I_{Sensor}) and sensor H_2/air current gain measured at V_{Sensor} = 0.9 V with I_H = 110 mA under cyclic exposures to air/N_2/0.5% H_2 in N_2 (see text).

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.

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