

Influence of Interface States on High Temperature SiC Sensors and Electronics

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ABSTRACT

Silicon carbide based metal/oxide/semiconductor (MOS) devices are well suited for operation in chemically reactive high temperature ambients. The response of catalytic gate SiC MOS sensors to hydrogen-containing species has been assumed to be due to the formation of a dipole layer at the metal/oxide interface, which gives rise to a voltage translation of the high frequency capacitance voltage (C-V) curve. From *in-situ* C-V spectroscopy, performed in a controlled gaseous environment, we have discovered that high temperature (800 K) exposure to hydrogen results in (i) a flat band voltage occurring at a more negative bias than in oxygen and (ii) the transition from accumulation to inversion occurring over a relatively narrow voltage range. In oxygen, this transition is broadened indicating the creation of a large number of interface states. We interpret these results as arising from two independent phenomena – a chemically induced shift in the metal/semiconductor work function difference and the passivation/creation of charged states (D_{IT}) at the SiO_2/SiC interface. Our results are important for both chemical sensing and electronic applications. MOS capacitance gas sensors typically operate in constant capacitance mode. Since the slope of the C-V curve changes dramatically with gas exposure, we discuss how sensor-to-sensor reproducibility and device response time are influenced by the choice of operating point. For electronic applications understanding the environmentally induced changes in D_{IT} is crucial to designing drift-free MOS devices. Our results are applicable to n-type SiC MOS devices in general, independent of the specifics of sample fabrication.

INTRODUCTION

Metal/oxide/semiconductor (MOS) devices based on the wide bandgap semiconductor SiC are attractive for gas sensing and electronic device applications in harsh environments. Emissions control for both real time monitoring and feedback control of exhaust products in the automotive and energy sectors require sensors that can operate in chemically reactive high temperature environments. Turbines, automotive engines and power plants also require high temperature electronic components. The native oxide of SiC, SiO_2 , enables fabrication of field-effect devices with gate controlled modulation of the semiconductor carrier concentration. The wide bandgap of SiC allows for semiconductor device operation up to temperatures of 1200K. In addition, SiC is chemically stable in reactive environments. The performance of SiC MOS devices in these harsh, high temperature ambients will depend on the specific application as discussed below.

The operation of field-effect chemical sensors are dominated by electronic and chemical interactions at interfaces. In the case of a MOS structure these interfaces are the environment/metal interface, the metal/oxide interface and the oxide/semiconductor interface. In this paper we describe how reducing and oxidizing species modify the electronic interfacial properties of Pt/SiO₂/SiC devices at high temperature. These results are obtained by *in-situ* capacitance-voltage (C-V) spectroscopy performed under sensor operating conditions.

High temperature chemical sensors based on refractory metal gate SiC devices have been demonstrated by a number of groups [1-7]. These include hydrogen, hydrocarbon and ammonia sensors operating at temperatures from 600K to 1300K. Specific sensor configurations [8] have achieved millisecond time response and sensitivity at the 0.1% level. Reference 1 reports on the failure free operation of CO, NO_x and O₂ sensors for six months in the exhaust stream of a power plant boiler. These measurements indicate that SiC based MOS chemical sensors have the potential to operate in real world industrial settings. To address the issues of reliability, stability and sensitivity, we report here on a detailed experimental study of hydrogen sensing following dehydrogenation at the heated catalytic gate in simulated exhaust environments.

The response of Si based catalytic gate MOS sensors operating at temperatures below 500K to hydrogen-containing species has been shown to be due to the formation of a polarized layer at the metal/oxide interface, which gives rise to a voltage translation of the high frequency capacitance voltage (C-V) curve [9]. The voltage shift in these devices is a measure of the reduction of metal/insulator workfunction difference (Φ_{MI}) in hydrogen. Similarly, the response of SiC based devices operating at elevated temperatures to hydrogen containing gases has been assumed to be entirely due to chemically modification of the metal/insulator barrier height. We show that at 800 K an additional mechanism contributes to the hydrogen sensitivity, namely the reversible passivation/creation of charged states at the oxide/semiconductor interface.

EXPERIMENTAL DETAILS

The Pt/SiO₂/SiC sensors were fabricated on n-type 6H-SiC wafers from Cree [10]. A 5 μm epitaxial layer with a nominal doping of $1.6 \times 10^{16} \text{ N/cm}^3$ was grown on 3.5° miscut highly doped $5 \times 10^{18} \text{ N/cm}^3$ wafers. The wafers were cut into 1 cm squares and stripped of the native oxide. The square samples were oxidized at 1150 $^\circ\text{C}$ in wet O₂ followed by an *in-situ* Ar anneal and wet reoxidation at 950 $^\circ\text{C}$ [11]. The oxide thickness is 43 nm as determined by spectroscopic ellipsometry. Prior to gate metallization the samples were cleaned in two RCA solutions of hydrogen peroxide with ammonia or hydrochloric acid, respectively. Circular dots of platinum, nominally 100 nm thick, were deposited through a shadow mask via e-beam evaporation at 350 $^\circ\text{C}$ in a 10^{-8} torr background pressure. Each sample contains an array of 10 to 20 capacitors with gate diameters ranging from 50 μm to 1000 μm . The Pt films are deposited directly on oxidized SiC substrates without the need of an interfacial silicide as used by other groups [1]. Our films adhere well to the substrate following repeated cycling to 600 $^\circ\text{C}$ [12]. Prior to electrical characterization, the oxide on the back of the sample was stripped and the sample was then glued with silver paste onto an alumina header with gold pads. The glue is electrically conducting and can withstand temperatures in air up to 730 $^\circ\text{C}$. Electrical contact between the Pt gates and the gold pads on the alumina were made by wire bonding 25 μm diameter gold wires at 350 $^\circ\text{C}$.

The samples were characterized via capacitance-voltage spectroscopy in a furnace with a controlled gas atmosphere. Contact to the gate was made by bonding an additional gold wire to the gold pad on the alumina header, then attaching the far end of the gold wire to the center conductor of the coaxial cable leading out of the furnace. The measurement system allows for four-terminal electrical measurements with better than pA and pF sensitivity up to temperatures of 600 °C. Simultaneous quasi-static and 1 MHz C-V characteristics were measured with a Keithley 595 quasi-static and 590 high-frequency meter. The gaseous ambient in the furnace tube can be controlled to the ppm level. Measurements were made using 99.999% purity pure nitrogen, mixtures of 10.3 % hydrogen in nitrogen, or 99.99% purity mixtures of 1.0 % oxygen in nitrogen. Typical gas flow rates were 400 ml/min.

RESULTS AND DISCUSSION

A schematic of our catalytic gate SiC field-effect sensor for hydrogen containing species is shown in Fig. 1. Refractory metal gates such as Pt, Pd and Ir can efficiently dehydrogenate long chain hydrocarbons at temperatures above 700K. Following dehydrogenation at the heated gate, hydrogen diffuses into the structure. At these temperatures the diffusion time for hydrogen through 100 nm of Pt and 43 nm of SiO₂ is less than 5 μs [13] and 0.5 ms [14] respectively. We demonstrate via *in-situ* C-V spectroscopy of Pt/SiO₂/SiC sensors at 800K (see Fig. 2) that oxidizing species affect the electronic properties of both the metal/oxide and oxide/semiconductor interfaces.

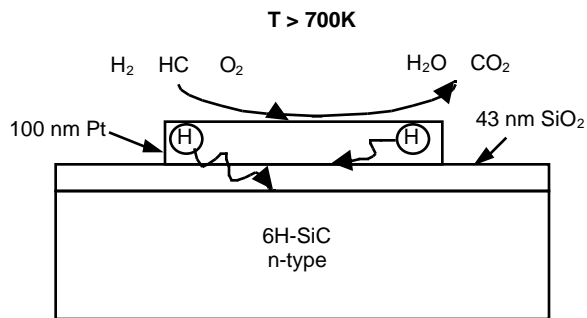


Fig. 1 Schematic of a catalytic gate SiC field-effect sensor for hydrogen containing gases. Typical operation is at $T > 700\text{K}$. Hydrogen can diffuse to both the metal/oxide and oxide/semiconductor interfaces.

Fig. 2 shows the high frequency C-V characteristic of a sensor at 800K in a hydrogen (10% H₂ in N₂) and an oxygen (1% O₂ in N₂) ambient. Exposure to hydrogen results in (i) a flat band voltage occurring at a more negative bias than in oxygen and (ii) the transition from accumulation to inversion occurring over a relatively narrow voltage range. In oxygen, this transition is broadened indicating the creation of a large number of interface states. From Terman analysis of the data [7] we find that the C-V characteristic in hydrogen represents that of a near ideal device, free of interface states, within the uncertainty of our measurements. However in oxygen the interface state density (D_{IT}) is a function of the position of the Fermi energy (E_F) in the bandgap. Near mid-gap the density is low, corresponding to a gate bias in the

lower portion of the C-V curve. The density increases as E_F is swept from mid-gap towards the conduction band edge, corresponding to a gate bias in the upper portion of the C-V curve.

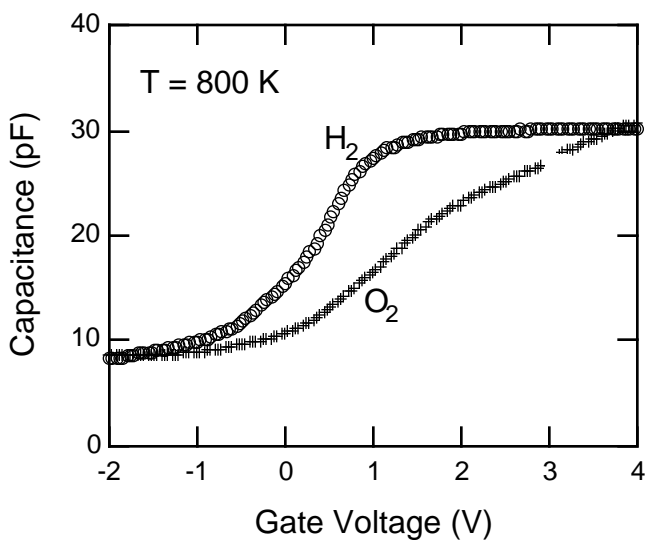


Fig. 2 High frequency (1 MHz) capacitance of a sample with a gate area of $3.8 \times 10^{-8} \text{ m}^2$ and an oxide thickness of 43 nm, measured in two gas environments, 10% H_2 in N_2 and 1% O_2 in N_2 . The gate voltage is swept from positive to negative voltages at 0.08 V/s.

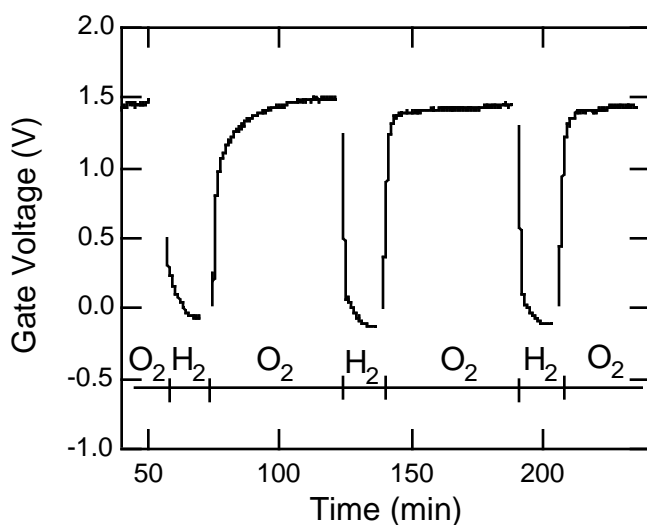


Fig. 3 Sensor measurements on the sample from Fig. 2 at 800 K. The capacitance is held constant at 20 pF and the gate voltage is recorded as the sensor signal during gas cycling. The sensor is exposed to 10% H_2 in N_2 and 1% O_2 in N_2 , separated by short exposures to pure nitrogen.

To operate the device as a gas sensor the capacitance is held at a constant value while modulating the gas composition. The resulting gate bias is then recorded as the sensor signal. Shown in Fig. 3 are sensor measurements from the device in Fig. 2, at a 20pF capacitance set point. The device was exposed to cycles of 1% O₂ in N₂ in and 10% H₂ in N₂ with short pulses of pure nitrogen in between (data omitted for sake of clarity). Over the three cycles the sensor response to reducing and oxidizing ambients is repeatable. There are several time constants evident in the data. We estimate that it takes about 1 min to exchange the gas in the vicinity of the sample and on the order of 5 minutes to exchange the gas in the furnace tube. Therefore we are not able to resolve the intrinsic response time of the SiC sensor, which has been shown to be as short as milliseconds [8]. We ascribe the ~5min time constant in switching from oxygen to hydrogen to the gas exchange system. The long, ~30min, response in switching from hydrogen to oxygen is due to charged states at the oxide/semiconductor interface, as discussed below.

High temperature operation of MOS devices places severe demands on the stability of the dielectric as well as the oxide/semiconductor interface. The interface state density of our samples [7] was determined from simultaneous quasi-static and 1 MHz C-V measurements at 300K and 500K in an inert nitrogen atmosphere. From high-low analysis of the data we determine interface state densities of $10^{12} < D_{IT} < 5 \times 10^{11}$ states/cm²-eV in the energy range $0.3 \text{ eV} < E_C - E < 0.9 \text{ eV}$. These values are comparable to thermally grown oxides with a wet reoxidation at 950 °C [11] used for SiC based electronic applications. Our use of platinum as a gate metal does not adversely effect D_{IT} as compared to more standard metallizations such as poly-silicon or aluminum.

We interpret the results of Fig. 2 and 3 as arising from two independent phenomena - a chemically induced shift in the metal/insulator workfunction difference and the passivation/creation of charged states at the oxide/SiC interface. At temperature above 700K the diffusion of hydrogen in and out of the Pt/SiO₂/SiC capacitor is rapid on the time scale of the sensor response. Hydrogen is present at both the environment/metal and oxide/semiconductor interfaces. In a reducing environment, hydrogen passivates the charged defects at the oxide/SiC interface. The sensor response is due entirely to a reduction in the metal/insulator barrier height, independent of the capacitance value. In an oxidizing environment, the hydrogen concentration at the oxide/semiconductor interface is decreased leaving behind negatively charged states at the interface. The interface state density is small near midgap and large in the upper portion of the C-V curve with slow response times [7]. The capacitance setpoint then determines the device response to oxidizing and reducing gases. In the upper portion of the C-V curve the slow large signal is due to both Φ_{MI} and D_{IT} . Whereas near midgap, the response is dominated by the metal/insulator workfunction difference. The sensor in Fig. 3 is biased in a regime where both mechanisms are operational as evidenced by the slow tail in switching from hydrogen to oxygen. Although we have focused on purely reducing or oxidizing environments, our results are applicable to high temperature sensing of hydrogen containing species in general, such as long chain hydrocarbons.

The stability of the sensor characteristic at high temperature was investigated by measuring the 1 MHz C-V curves in hydrogen of the device in Fig. 2 before and after 330 minutes of sensor operation (see Fig. 4). During this period the device was maintained at 800K while modulating between reducing and oxidizing gas ambients. Note that a fixed positive gate bias of 0.44 V has been added to the 330 min data. We attribute this shift to a build up of negative charge in the oxide during sensor operation. The shape of the C-V curves in hydrogen

at 800K before and after sensor measurements are very similar indicating that the effect of hydrogen passivation of the states at the oxide/semiconductor interface is reversible.

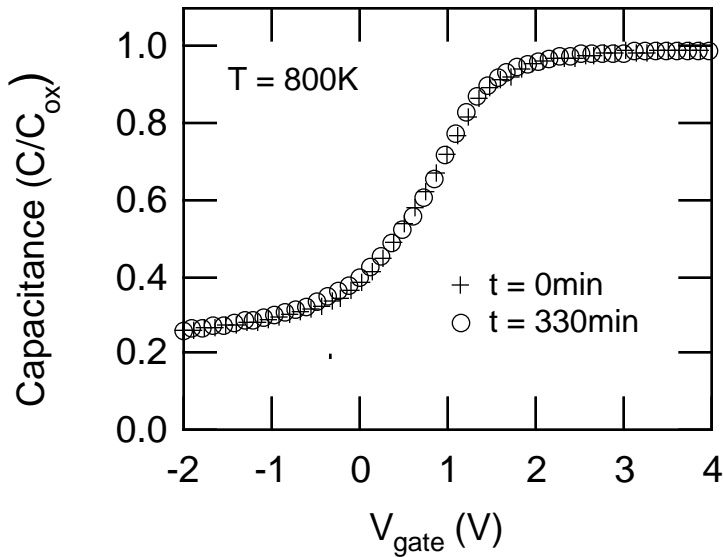


Fig. 4. 1 MHz C-V characteristic of the device from Fig. 2 at 800K in a 10% H₂ in N₂ ambient. The crosses are the initial C-V curve and the circles are the C-V curve taken after 330 min of sensor operation at 800K.

It is desirable that the sensor response be repeatable from device to device. The measured values of interface state density depends critically on the specific details of the oxidation process as well as post oxidation processing. We propose therefore that for sensor-to-sensor repeatability that the optimum bias point is near midgap. In addition this bias point should also result in fast sensor response times by minimizing the effect of slow interface states. Note that long term operation of SiC MOS sensors in flue gases was been previously reported [1].

We have observed the reversible passivation/creation of charged states at the oxide/SiC interface in cycling between hydrogen/oxygen ambients in a number of different, independently fabricated samples. These include samples with Pt gates deposited at 350 °C via both e-beam evaporation and sputtering in a 5 mtorr Ar ambient. The thermal oxide was grown at 1150 °C in wet O₂ followed by an *in-situ* Ar anneal and wet reoxidation at 950 °C [11], or at 1200 °C in dry ambient followed by a wet reoxidation at 950 °C [15]. The substrate was either a 6H-SiC or 4H-SiC highly doped n-type wafer with a low doped n-type epitaxial layer. These results are applicable therefore to n-type field-effect SiC devices in general. For high temperature SiC based electronic devices understanding the environmentally induced changes in D_{IT} is crucial to designing drift-free MOS devices.

CONCLUSIONS

The response of catalytic gate MOS field-effect SiC sensors to oxidizing and reducing gases at 800K is due to two independent phenomena: the reduction of the metal/oxide barrier height in hydrogen and the creation/passivation of charged states at the oxide/semiconductor interface. For n-type devices these states are located primarily in the upper half of the bandgap. The choice of set point, for capacitively biased sensors, determines both the magnitude of the sensor signal and the relative contribution of each mechanism towards the sensor response. In terms of both sensor response time and sensor-to-sensor repeatability we show that the optimum bias point is near midgap. Our results on the reversible passivation/creation of states at the oxide/SiC interface are applicable towards the design of stable, high temperature chemical sensors and electronic devices based on field-effect metal/oxide/SiC structures.

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