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SiC Field-Effect Devices Operating at High Temperature

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Field-effect devices based on SiC metal-oxide-semiconductor (MOS) structures are attractive for electronic and sensing applications above 250°C. The MOS device operation in chemically corrosive, high-temperature environments places stringent demands on the stability of the insulating dielectric and the constituent interfaces within the structure. The primary mode of oxide breakdown under these conditions is attributed to electron injection from the substrate. The reliability of n-type SiC MOS devices was investigated by monitoring the gate-leakage current as a function of temperature. We find current densities below 17 nA/cm^2 and 3 nA/cm^2 at electric field strengths up to 0.6 MV/cm and temperatures of 330°C and 180°C, respectively. These are promising results for high-temperature operation, because the optimum bias point for SiC MOS gas sensors is near midgap, where the field across the oxide is small. Our results are valid for n-type SiC MOS sensors in general and have been observed in both the 4H and 6H polytypes.

Key words: SiC, metal-oxide-semiconductor (MOS) devices, high temperature, reliability, semiconductor-insulator interface, sensor

INTRODUCTION

Field-effect devices based on SiC metal-oxide-semiconductor (MOS) structures are attractive for electronic and sensing applications above 600 K, which represents the upper bound for Si-based structures.[1] We are investigating insertion opportunities for SiC sensors and electronics in energy plants for both real-time monitoring and control of exhaust products. The wide bandgap of SiC enables device operation to temperatures in excess of 1,200 K. In the case of the 6H polytype, the energy gap is 3.0 eV, compared to 1.1 eV for silicon. Field-effect structures require a robust dielectric to modulate the semiconductor carrier concentration via an applied gate potential. Silicon carbide has a thermal oxide, SiO_2, which fulfills this need. In addition to high temperatures (up to 1,050 K), emissions monitoring in power plants requires devices that can withstand high pressures and reactive gases, such as hydrocarbons and sulfur oxides. Silicon carbide is chemically stable in reactive environments and provides a platform for harsh environment sensors as well as the supporting control electronics.

The operation of field-effect devices is dominated by electronic 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. For SiC MOS technology to fulfill its potential in real world applications, the issues of reliability and stability need to be addressed. In this paper, we investigate the high-temperature reliability of the gate dielectric and discuss our results in terms of the conduction band alignment between silicon dioxide and the various SiC polytypes. We also examine the stability of the metal-oxide interface by monitoring the adhesion of the metal gates during high-temperature thermal cycling.

A schematic of our catalytic-gate SiC field-effect sensor for hydrogen-containing species is shown in Fig. 1. Following dehydrogenation at the heated catalytic gate, the chemical event is detected electronically via a change in the device potential. Hydrogen diffuses into the sensor modifying the charge distribution in the MOS device, and the resultant change in device potential is then measured via the field effect. In the case of our capacitive device, the presence of the hydrogen-containing species shifts the sensor's capacitance-voltage (C-V)

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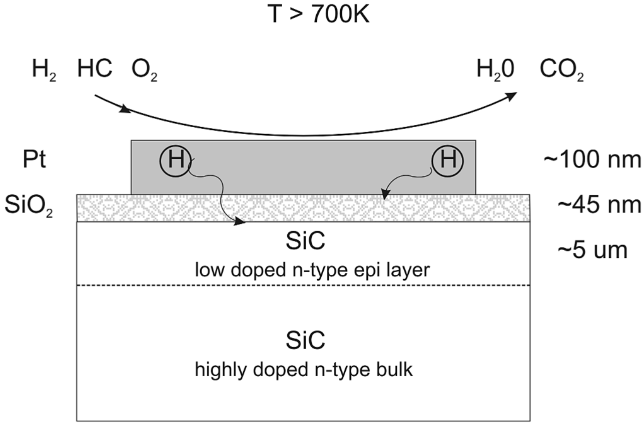

Fig. 1. Schematic of a catalytic-gate SiC field-effect sensor for hydrogen-containing gases. Typical sensor operation is at T > 700 K. Gate-leakage current measurements were performed on the same structure, and Table I lists the details for the devices used in the high-temperature reliability study.

characteristic toward negative potentials. A review of refractory metal-gate SiC sensors for high-temperature chemical applications can be found in Ref. 2. This review describes hydrogen and hydrocarbon sensors operating at temperatures from 600 K to 1,300 K. Specific sensor configurations have also achieved millisecond time response and sensitivity at the 0.1% level. The fast response makes the sensors suitable for feedback control in automotive internal-combustion engines and electric-power generation turbines.

From detailed measurements of the sensor response mechanism, we have previously determined that the optimal operating point for SiC MOS-based sensors in terms of response time and device-to-device repeatability is near midgap.[3] For MOS devices, the primary function of the gate dielectric is to block the flow of charge between the gate and the conducting channel at the oxide-semiconductor interface. Therefore, a measure of the oxide reliability is obtained by monitoring the gate-leakage current as a function of temperature. In this paper, we show that biasing the sensor at midgap minimizes the oxide leakage current, thereby significantly improving high-temperature device reliability. We investigate the validity of these results for SiC, n-type, field-effect sensors in general, focusing on the 4H and 6H polytypes.

EXPERIMENTAL

Device Fabrication

The refractory metal-gate SiC MOS devices (Fig. 1) were fabricated on commercially available, highly doped (1–11 × 10^{18} N/cm^3), n-type wafers with a low doped (1–2 × 10^{16} N/cm^3), 3–5-μm epitaxial layer. Both the 4H and 6H polytypes were used. The specific details of the samples used for the high-temperature gate-leakage measurements are given in Table I. The wafers were cut into 1-cm squares and stripped of the native oxide. An oxide 40–50-nm thick was grown on the square samples via either a “wet/reox” or “dry/reox” process. Wet/reox refers to oxidation at 1,150°C in wet O_2, followed by an in-situ Ar anneal and wet reoxidation at 950°C, whereas dry/reox refers to dry oxidation at 1,200°C, followed by a 950°C wet reoxidation.[4] The precise oxide thickness was determined by spectroscopic ellipsometry to within 1 nm.

The interface between the gate metal and the dielectric is critical for both metal adhesion and gas sensing. Prior to metallization, the samples were cleaned in two RCA solutions in a class 100 cleanroom. First, we use a solution of concentrated NH_3, 30%-H_2O_2, and H_2O (1:1:6) at 75°C for 20 min and a distilled water rinse, followed by in a solution of concentrated HCl, 30%-H_2O_2, and H_2O (1:1:7) at 75°C for another 20 min. After a long rinse in distilled water, the samples were stored in deionized water until immediately prior to metal deposition. The CMOS-grade chemicals were obtained from J. T. Baker (Mallinckrodt Baker, Inc., Phillipsburg, NJ). Arrays of circular Pt or Ti/Pt dots, ranging in diameter from 50 μm to 1,000 μm, were e-beam evaporated or sputter deposited through a shadow mask. In the case of the sputtered samples, the base chamber pressure was 3×10^{-8} torr, and Pt was sputtered at 350°C in a 5-mtorr Ar atmosphere. The e-beam samples were also evaporated at 350°C in a 10^{-8} torr chamber. The nominal gate thickness was 100 nm. One of the samples used for the gate-leakage measurements was only 15-nm thick; it was originally designed for a related photoemission experiment.[5]

A common back contact to the entire array of devices on the 1-cm^2 sample was made by stripping off the back oxide in CMOS-grade buffered HF, then attaching the sample with a conducting silver

Table I. Details of the Four Different Samples Used to Investigate High-Temperature Sensor Reliability

		Epitaxial Layer		Gate Oxide		Gate Metal	
Sample	Bulk Doping (×10^{18} N/cm^3)	Doping (×10^{16} N/cm^3)	Thickness (μm)	Growth Technique	Thickness (nm)	Type	Thickness (nm)
6H-1	1.01	2.1	3	Wet/Reox	49.2	Sputtered Ti/Pt	2/100
6H-2	1.01	2.1	3	Wet/Reox	47.2	Sputtered Pt	15
4H-1	11.0	1.3	5	Dry/Reox	49.4	Sputtered Pt	100
4H-2	11.0	1.3	5	Dry/Reox	40	E-beam Pt	100

The SiC bulk and epitaxial layers are all n-type (doped with nitrogen). Two oxidation processes were used: dry/reox and wet/reox (see text for details). A cross-sectional view of an individual sensor is shown in Fig. 1.

paste onto an alumina header with gold pads. Electrical contact to the Pt gates was made with Pt probe tips for the leakage measurements. For C-V characterization, gold wire was bonded at 350°C between the Pt gate and the gold pad on the alumina header.

High-Temperature Characterization Techniques

The gate-leakage measurements were made in air using a commercial current-voltage (I-V) characterization system.[6] The samples were placed inside a shielded probe station with a temperature-controlled chuck that can be heated up to 600 K. To make $\pm$2-pA measurements at high temperature, care was taken to electrically isolate the SiC sample mounted on its alumina header from the heater coils of the hot chuck. At a given temperature, both I-V and C-V (1-MHz C-V) scans were taken for each device. The gate-leakage characteristic as a function of gate voltage was obtained by subtracting out the “probe up” current from the I-V characteristic. The leakage-current density was evaluated at a gate voltage corresponding to the capacitor being biased at midgap as follows. First, we calculated the midgap capacitance from the measured device area, oxide thickness, and doping density of the epitaxial layer (obtained from $1/C^2$ analysis of the C-V curve in depletion). Then, using the measured C-V characteristic, we obtained the midgap voltage.

For sensor measurements in hydrogen and oxygen, the devices were characterized via C-V spectroscopy in a furnace with a controlled gas atmosphere. Contact to the Pt sensing gate was made by bonding an additional gold wire to the gold pad on the alumina header, then attaching the opposite end of the gold wire to the center conductor of the coaxial cable leading out of the furnace. In our sensor testing system, we can make four-terminal electrical measurements with better than pA and pF sensitivity up to temperatures of 900 K. A commercial measurement setup was used to obtain the 1-MHz C-V characteristics in hydrogen and oxygen.[6] The ambient gas in the furnace tube can be controlled to the parts per million level. Measurements were made using 99.999% nitrogen, mixtures of 10.3% hydrogen (99.999%) in nitrogen, or mixtures of 1.0% oxygen (99.99%) in nitrogen. Typical gas flow rates were 400 ml/min.

RESULTS AND DISCUSSION

SiC Field-Effect Gas Sensors

A schematic of our SiC field-effect sensor for hydrogen-containing species is shown in Fig. 1. The sensor is a capacitor structure with a catalytically active gate electrode. At temperatures above 700 K, refractory metal electrodes, such as Pd, Pt, and Ir, can efficiently dehydrogenate long-chain hydrocarbons. Following dehydrogenation at the heated gate, hydrogen diffuses into the structure reaching both the metal-oxide and oxide-SiC interfaces in less than 0.5 ms.[7] The chemical event at the sensing gate electrode is detected electronically by a change in the device potential.

To characterize the sensor performance in situ, we have developed a setup to make four-probe electrical measurements with better than pA and pF sensitivity in a controlled gas environment up to 900 K. Shown in Fig. 2 is the C-V characteristic of a SiC gas sensor operating at 800 K in hydrogen (10% H_2 in N_2) and oxygen (1.0% O_2 in N_2). The device is a n-type capacitor fabricated on a 6H-SiC substrate (5-μm thick, 1.6×10^{16} N/cm^3 epitaxial layer) with a 43-nm-thick gate oxide (grown via wet oxidation) and a 100-nm-thick Pt sensing gate layer. In hydrogen, we observe a negative flat band shift and a near ideal C-V characteristic with no trapped charge at the oxide-semiconductor interface within our measurement accuracy.[8] In oxygen, the C-V characteristic has a positive flat band shift. In addition, the transition from accumulation to inversion is significantly broadened, which indicates the existence of charge at the oxide-semiconductor interface in an oxygen atmosphere. We have found that the interface state density is a function of the position of the Fermi energy at the interface.[8]

During sensor measurements, the device is biased in a constant capacitance mode (via a feedback circuit), while the ambient gas concentration is modulated. The gate voltage required to maintain the capacitance set point is then recorded as the sensor signal. From extensive measurements in hydrogen and oxygen, we have determined that there are two mechanisms that contribute to the sensor response.[3] The first is the chemically induced change in the metal-insulator barrier height. The second mechanism is the passivation in hydrogen and the

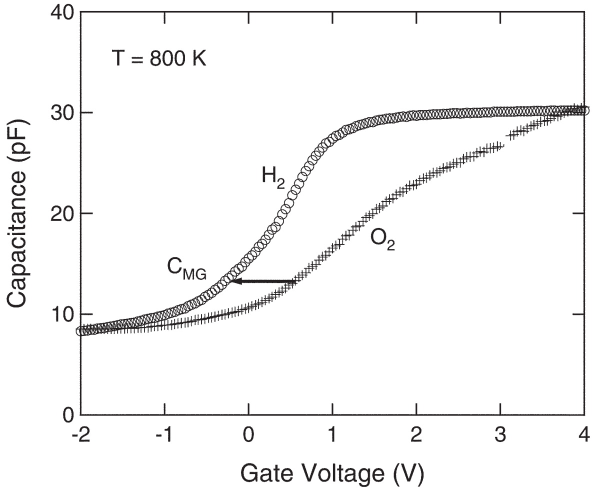

Fig. 2. Capacitance-voltage characteristic (1 MHz) of a SiC gas sensor at 800 K in hydrogen and oxygen. To operate the device as a sensor, the capacitance is held constant while monitoring the gate voltage as the sensor output. Two independent mechanisms contribute to the sensor signal: (a) chemical modification of the metal-insulator barrier height and (b) charging and passivation of states at the oxide/SiC interface. The optimum-sensor bias is at midgap.

creation in oxygen of charged states at the oxide-SiC interface. The relative contribution of the two mechanisms is determined by the capacitance set point. In addition, the time scale for the environmentally induced defects is significantly longer than the barrier height shift. Therefore, for optimum-sensor performance, the sensor should be biased in such a manner that the first mechanism dominates. We have shown that the optimum set point for a SiC MOS sensor with respect to response time is close to midgap.[3]

These results are applicable for SiC field-effect sensors in general. We have fabricated SiC MOS capacitors via a number of different processing techniques including sputtered and e-beam deposited gates, wet- and dry-gate oxidations, and on 4H-SiC and 6H-SiC substrates. In all of these cases, the reversible passivation-creation of charged states at the SiO_2-SiC interface in cycling between hydrogen and oxygen was observed at temperatures above 700 K. One of the primary applications of SiC field-effect devices is in high-temperature environments where Si-based MOS devices cannot operate. At these temperatures, any residual oxygen in the environment would result in the creation of interface states. The measured values of interface state density depends critically on the specific details of the oxidation process as well as post-oxidation processing. This introduces a lack of repeatability in devices fabricated at different times. To minimize the effects of interface state density and maximize device-to-device repeatability, we propose that SiC field-effect sensors should be biased near midgap.

Optimum-Sensor Operating Point

The SiC MOS device operation in chemically corrosive, high-temperature environments places stringent demands on the stability of the insulating dielectric and the constituent interfaces within the structure. The primary mode of oxide breakdown at elevated temperatures is attributed to electron injection from the substrate.[9,10] The band alignment between SiO_2 and different polytypes of SiC as well as Si has been investigated using internal photoemission techniques.[11] Results are summarized in Fig. 3.

At present, the majority of SiC devices are fabricated on 4H and 6H substrates because of the commercial availability of these wafers. Both 4H-SiC and 6H-SiC have a larger bandgap than Si. However, as Fig. 3 shows, the alignment of the conduction bands is such that there is actually a smaller barrier toward electron injection from the conduction band of the semiconductor into the insulator for these two SiC polytypes than in the case of Si. To minimize the deleterious effects of oxide breakdown, it would be advantageous to operate the MOS device in a regime where electron injection into the oxide is minimized. For n-type capacitors, this occurs when the Fermi energy at the oxide-semiconductor interface is in the lower half of the bandgap, i.e., midgap and below. However, for sensor operation, we need to operate in a region of the C-V characteristic (Fig. 2), which has a large slope, because we are using the device in a constant capacitance mode. This requirement is fulfilled between midgap and weak accumulation. The region near midgap represents a compromise between the preceding two requirements. Therefore, we propose that biasing near midgap is the optimum sensor operating point with respect to long-term device reliability at high temperatures. For our n-type SiC MOS structures biased at midgap, we compute electric field strengths below 0.6 MV/cm at temperatures up to 600 K.

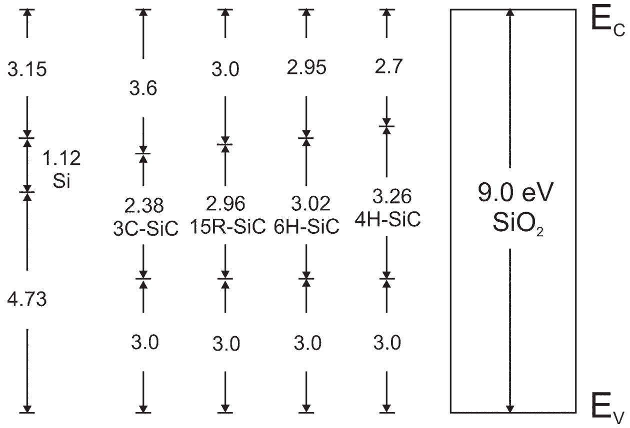

Fig. 3. Band alignment of the interface between SiO_2, Si, and SiC showing the conduction band offset between SiO_2 and the various semiconductors.[11]

High-Temperature SiC MOS Device Reliability

To investigate the reliability of SiC MOS structures at elevated temperatures we fabricated devices using several different techniques; the specific details of the four different samples are listed in Table I. Capacitors were fabricated on both the 6H and 4H polytypes. Two different oxidation techniques were used: (a) wet/reox, which refers to oxidation at 1,150°C in wet O_2, followed by an in-situ Ar anneal and wet reoxidation at 950°C and (b) dry/reox, which refers to dry oxidation at 1,200°C, followed by a 950°C wet reoxidation.[4] The metal gate was deposited at 350°C via either e-beam or sputter deposition.

Gate-Leakage Current Measurements at High Temperature

The gate-leakage current as a function of gate voltage and temperature was measured from room temperature to 600 K in air. The current density was then evaluated at the midgap gate bias. Only the higher temperature results above 450 K are shown in Figs. 4 and 5. The current density for four different gates, fabricated on two separate 6H-SiC samples, and from three gates, fabricated on two different 4H-SiC samples, are shown in Figs. 4 and 5, respectively. The error bars in both figures do not

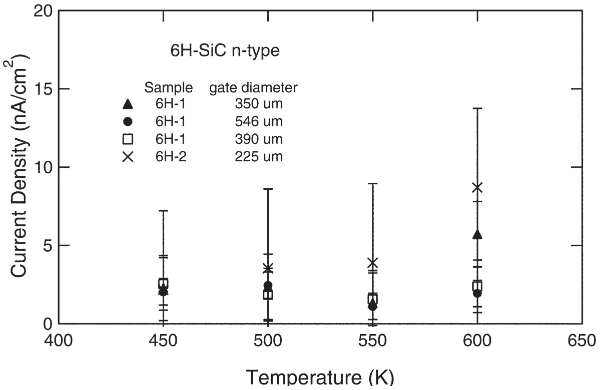

Fig. 4. Gate-leakage current density as a function of temperature for 6H-SiC n-type devices. Table I shows details of the device geometry. The capacitor is biased at midgap to optimize device reliability at high temperature.

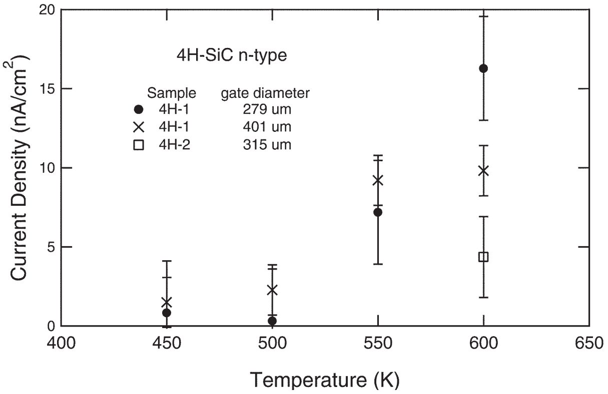

Fig. 5. Gate-leakage current density as a function of temperature for 4H-SiC n-type devices. Table I shows details of the device geometry. The capacitor is biased at midgap to optimize reliability at high temperature.

reflect the device quality, rather they are due to the ±2-pA measurement uncertainty on the hot chuck. Below 500 K, the leakage current is approximately constant and begins to increase between 550 K and 600 K. Note that the electric field across the oxide at midgap for all the devices is low, <0.6 MV/cm up to 600 K. Within our small measurement set, no correlations between gate diameter, metallization technique, or gate material, oxidation method, or oxide thickness were observed.

Two groups have recently reported on the reliability of "state-of-the-art" thermal oxides grown on n-type 4H-SiC substrates. The MOS capacitors with mean time to failure of >10 h at a field of 7 MV/cm at 570 K were reported.[12] Extrapolating these results to the electric field of our MOS sensors biased at midgap, corresponds to well over 100-year operation at 570 K. Note that the authors considered a capacitor failed when the gate-leakage current exceeded 1 μA. In Figs. 4 and 5, the highest current level of any of our devices at 600 K is 12 pA, significantly below the breakdown threshold. A second group has reported on room-temperature measurements of leakage-current densities below 1 nA/cm^2 for oxide fields up to 6.5 MV/cm.[13] An important difference between our devices and the gate oxidation process used by both these groups is the addition of a high-temperature nitridation process immediately following dry thermal oxidation. Nitridation has been shown to significantly decrease the interface state density near the conduction band edge of 4H-SiC.[14] For n-type 6H-SiC MOS capacitors operating at 725 K, current densities <100 nA/cm^2 (for oxide fields up to 8.9 MV/cm) and a 12 MV/cm dielectric breakdown strength have been reported.[15] The gate dielectric of these devices included a Si_3N_4 layer.

High wear on the gate oxide leads to massive changes in the C-V characteristic, ultimately resulting in sensor failure, so such conditions need to be avoided. Our results shown in Figs. 4 and 5 are very encouraging in terms of the reliability of SiC MOS sensors at elevated temperatures. For oxide fields below 0.6 MV/cm, we obtain current densities <10 nA/cm^2 and <17 nA/cm^2 at 600 K for the 6H and 4H polytypes, respectively. In our experience (from a measurement set of 100 devices), capacitors with low leakage-current densities at 600 K always have correspondingly low leakage-current densities (±2 pA, which is at our noise level) at room temperature. Additionally, from sensor measurements at 600–800 K on a handful of devices, we can infer the gate-leakage current and find that they follow the same trend. From these results, we extrapolate that low leakage-current density at 600 K will lead to devices with low leakage-current density at the sensor operating temperatures above 700 K. Note that the oxide leakage data shown in Figs. 4 and 5 were limited by our experimental setup to 600 K and below. Plans are underway to extend these measurements above 700 K (up to 900 K) using platinum microheaters.[5]

Biasing at midgap significantly reduces the field across the gate oxide, which in turn lowers the oxide current, resulting in longer device lifetimes at higher temperature. Our results are independent of gate diameter, which ranged from 220 μm to 550 μm, indicating that edge effects play a minor role. Note that, at high temperature, our 4H-SiC results are similar to those obtained for 6H-SiC. Power electronics applications currently favor the 4H polytype because of its higher electron mobility.

Metal-Gate Stability During Temperature Cycling

The stability of the sensing gate metal during repeated temperature cycling is another important parameter that will determine the long-term reliability of SiC devices. Toward this end, we have focused our efforts on obtaining a sharp and reproducible metal-oxide interface without the use of additional interfacial layers. Our procedure is to clean the samples prior to metallization using the standard RCA technique in a class 100 clean room, then deposit the Pt film under quasi-ultrahigh vacuum (UHV) conditions at 620 K. The adhesion of the metal films was checked by two different temperature-cycling measurements. Four-point probe measurements were performed on large-area (~9 mm × 9 mm) Pt films deposited on an oxidized SiC substrate. The temperature-dependent resistivity of the film up to 900 K in air was consistent with that of bulk Pt. In the second experiment, the films were cycled several times by heating rapidly to 1,100 K in a UHV chamber. No signs of delamination or changes in morphology were observed after either of the temperature cycling experiments. Scanning electron micrographs of 100-nm-thick, e-beam deposited and sputtered Pt gates showed ~100-nm-size individual grains in both films. We have previously shown[3] that the C-V characteristic of our SiC sensors is unchanged following 4 h of sensor measurements, which consisted of continuous cycling between O_2 and H_2 at 700 K. This indicates that cycling between reducing and oxidizing environments at high temperature does not adversely affect the electrical response of the sensor. We are in the process of investigating the effects of frequent temperature cycling on the electrical characteristics of the sensors to complete our study of the stability of the metal gates.

CONCLUSIONS

We have investigated the reliability of n-type, SiC field-effect sensors on 4H and 6H substrates in terms of the high-temperature stability of the dielectric layer and the gate metallization. The Pt sensing gate was mechanically stable under repeated cycling up to 1,100 K. The optimum sensor bias point in terms of device-to-device repeatability and high-temperature stability of the gate oxide is near midgap. The gate-leakage current density at 600 K was measured to be <10 nA/cm^2 and <17 nA/cm^2 for devices fabricated on the 6H and 4H polytypes, respectively. The leakage measurements were independent of specific device fabrication procedures, such as gate oxidation or metallization technique as well as gate size, which ranged from 220 μm to 550 μm in diameter. Our results are promising for the development of robust SiC MOS sensors for high-temperature applications.

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