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6.4: Interface States in High Temperature SiC Gas Sensing

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Abstract

Silicon carbide based metal-oxide-semiconductor (MOS) devices are attractive for gas sensing in harsh, high temperature environments. The response of catalytic gate SiC 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. 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 (high capacitance) to inversion (low capacitance) 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 at the SiO_2/SiC interface. MIS capacitance sensors typically operate in constant capacitance mode. These results affect sensor sensitivity since the slope of the C-V curve changes dramatically with gas exposure.

Keywords

SiC, sensor, interface states, silicon carbide

INTRODUCTION

Emissions control for the automotive and energy sectors requires gas sensors that can operate in chemically reactive high temperature environments for both real time monitoring and feedback control of exhaust products. Gaseous species that need to be monitored include hydrogen, hydrocarbons, nitrogen oxides and sulfur oxides. Metal/insulator/semiconductor (MIS) structures with catalytically active gates are widely used to electronically detect the presence of various chemical species [1, 2]. The wide bandgap semiconductor silicon carbide, SiC, enables device operation to temperatures in excess of 1200K. In the case of the 6H polytype the energy gap is 3.0 eV, compared to 1.1 eV for silicon. MIS devices require a robust dielectric to enable modulation of the semiconductor carrier concentration via an applied gate potential. SiC has a native oxide, SiO_2, which fulfills this need. In addition SiC is chemically stable in reactive environments making it well suited for sensing applications in harsh environments.

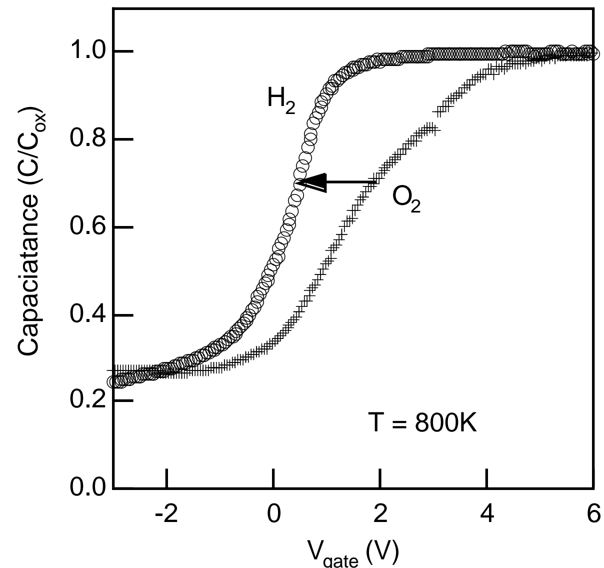

Figure 1. Capacitance-Voltage characteristic (1 MHz) of a catalytic gate SiC device at 800K. Operation in a reducing environment results in both a flat band shift (standard sensor response) and reversible annealing of SiO_2/SiC interface states.

The operation of field-effect devices is dominated by electronic interactions at interfaces. In the case of a MIS 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/SiO_2/SiC devices at high temperature. These results are obtained by *in-situ* capacitance-voltage (C-V) spectroscopy performed under sensor operating conditions (see Figure 1).

CATALYTIC GATE SILICON CARBIDE FIELD-EFFECT GAS SENSORS

Refractory metal gate SiC devices have been demonstrated for high temperature chemical sensing application by a number of groups [3-9]. These include hydrogen and hy-

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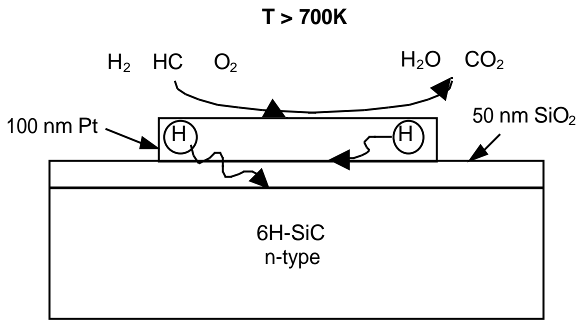

Figure 2. Schematic of a catalytic gate SiC field-effect sensor for hydrogen containing gases. Typical operation is at T > 700K. Hydrogen can diffuse to both the metal/oxide and oxide/semiconductor interfaces.

drocarbon sensors operating at temperatures from 600K to 1300K. Specific sensor configurations have achieved millisecond time response and sensitivity at the 0.1% level. In addition there are preliminary indications that suitably designed devices may offer sensitivity to ammonia, carbon monoxide, nitrogen oxides and fluorocarbons. For this technology to fulfill its potential in real world applications the issues of reliability, stability and sensitivity need to be addressed, which requires a detailed experimental study of hydrogen transduction following dehydrogenation at the heated catalytic gate.

A schematic of our catalytic gate SiC field-effect sensor for hydrogen containing species is shown in Figure 2. 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. For Si based catalytic gate sensors operating below 500K it has been shown that hydrogen gives rise to a dipole layer at the metal/oxide interface and to drifting charges in the oxide [10]. This chemically induced polarization charge results in a simple lateral shift of the C-V or current-voltage (I-V) characteristic of the capacitor or Schottky diode sensor, respectively. The magnitude of the voltage shift in these Si based sensors is a measure of the chemically modified metal/oxide workfunction difference (Φ_{MS}). It has been assumed that the same mechanism describes the operation of higher temperature SiC based sensors for hydrogen containing species. At temperatures above 700K the diffusion time for hydrogen through 100 nm of Pt and 50 nm of SiO_2 is less than 5 µs [11] and 0.5 ms [12] respectively. We demonstrate via *in-situ* C-V spectroscopy of Pt/SiO_2/SiC sensors at 800K (see Figure 1) that oxidizing species affect the electronic properties of both the metal/oxide and oxide/semiconductor interfaces.

EXPERIMENTAL

The Pt/SiO_2/SiC sensors were fabricated on n-type 6H-SiC wafers from Cree [13]. A 5 µm epitaxial layer with a nominal doping of 1.6 x 10^{16} N/cm^3 was grown on 3.5° miscut highly doped 5 x 10^{18} 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 °C in wet O_2 followed by an *in-situ* Ar anneal and wet reoxidation at 950 °C [14]. 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 °C in a 10^{-8} torr background pressure. Gate diameters range from 50 µm to 1000 µm. The Pt films, deposited directly on oxidized SiC substrates without the need of an interfacial silicide [2], adheres well to the substrate following repeated cycling to 600 °C [15]. 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 750 °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 °C.

The samples were characterized via capacitance-voltage spectroscopy, either on a regulated hot chuck in air or in a furnace with a controlled gas atmosphere. On the hot chuck, electrical contact to the gold pads on the alumina header was made with micro-positioner controlled tungsten probe tips. In the furnace, probe tips do not work reliably, probably because of the low spring forces at high temperatures. Instead, an additional gold wire was bonded to the gold pad. The far end of the gold wire was then glued to the wire that forms 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 100 KHz or 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 mixtures of 1.0 % oxygen in nitrogen, 10.3 % hydrogen in nitrogen or pure nitrogen. Typical gas flow rates were 400 ml/min.

INTERFACE STATE CHARACTERIZATION

We utilize capacitance-voltage spectroscopy to probe both the electronic properties of the interfaces within the Pt/SiO_2/SiC capacitors and to determine sensor functionality. As shown by the arrow in Figure 1, the sensor response to reducing and oxidizing ambients is obtained by biasing the device at a constant capacitance and monitoring the voltage needed to maintain that capacitance. By performing C-V spectroscopy at elevated temperatures in a controlled environment we determine how the presence of particular gaseous species affects the density of states at the SiO_2/SiC interface and within the oxide itself.

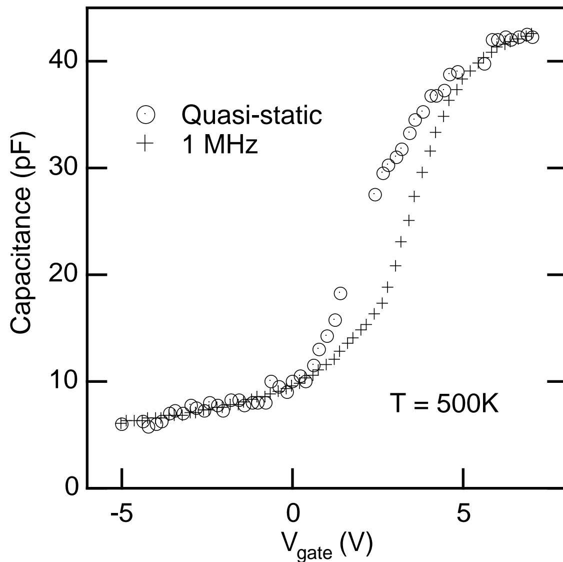

Figure 3. Quasi-static and 1 MHz capacitance-voltage characteristics in nitrogen at 500K.

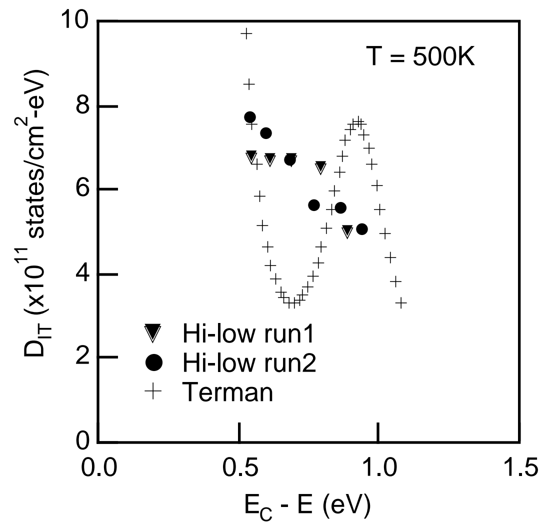

Figure 4. Interface state density at 500K in nitrogen obtained from both hi-low analysis (data in Figure 3) and Terman analysis. The discrepancy between the hi-low and Terman results is due to an artifact of the Terman analysis (see text).

Simultaneous hi-low technique

Figure 3 shows the high-frequency (1 MHz) and quasi-static C-V curves of a 260 µm diameter capacitor in nitrogen at 500K, measured simultaneously. For large positive gate voltages the n-type capacitor is biased in accumulation and both curves measure the oxide capacitance. Sweeping the gate bias towards negative voltages depletes the semiconductor of majority carriers at the oxide/semiconductor interface, so the series combination of oxide plus semiconductor capacitance is measured. Since these measurements were performed in the dark, the semiconductor does not invert at large negative biases but remains in depletion due to the slow minority carrier generation rate at 500K. The effect of charge accumulation in states at the oxide/semiconductor interface is seen in the quasi-static curves. Following the analysis of Nicollian and Brews [16] we assume that the interface states cannot follow the 1 MHz AC modulation, such that the 1 MHz characteristic represents the "ideal" C-V curve of the capacitor. For the quasi-static curve as the Fermi energy (E_F) is swept from the conduction band edge across the bandgap, an interface state in an energy width kT about E_F, can respond to the AC modulation resulting in a broadening of the C-V characteristic.

The interface state density (D_{IT}) obtained via hi-low analysis is shown with the solid symbols in Figure 4. The solid symbols represent the analysis from two sequential runs of the same device taken under identical conditions, from which we estimate a measurement uncertainty of ±10%. The range of energies within the semiconductor bandgap probed by hi-low analysis is determined by the response time of the interface states at the measurement temperature [17,18]. We estimate that at 500K using a DC sweep rate of 0.5V/s the valid energy range is 0.55 eV < E_c – E < 0.95 eV. The interface state density measurements in the upper half of the bandgap, E_c – E < 1.0 eV, are comparable to results obtained by other researchers [18] for similar thermally grown oxides with a 950 °C wet reoxidation anneal. Thus in the absence of reducing or oxidizing species the electronic properties of the Pt/SiO_2/SiC sensors are comparable to metal-oxide-SiC capacitors with "traditional" gate metallizations such as Al or poly-Si.

At temperatures above 500K we find that it is experimentally difficult to use the hi-low technique to determine D_{IT}. This is due to the increase in gate leakage current, > 1 pA, with increasing temperature. Although we are able to measure quasi-static curves up to 600K, random spikes in the gate current make the characteristics very noisy, rendering it difficult to obtain reproducible interface state density measurements using the hi-low techniques. Note that in Figure 3, at a gate bias of 2V the quasi-static capacitance is off scale due to a current spike. A study of the high temperature oxide reliability of SiC based MIS devices is presented in [19]. Despite the problems with the quasi-static measurements, we are able to obtain reproducible high-frequency C-V curves at temperatures up to 800K, which is well within the range of operation for catalytic gate field-effect sensors.

High-frequency (Terman) technique

The experimentally simplest method for obtaining the interface state density at the oxide/semiconductor interface is the high-frequency method developed by Terman [20]. It is also well suited to characterizing sensors, since the sensor response can be obtained from the high-frequency C-V curves in different gas environments. In the Terman technique a C-V characteristic is measured at a frequency high enough that the interface states can not follow the small

AC modulation. It is assumed that they can, however, follow the slow DC bias sweep. During the DC sweep, states in an energy range kT across from E_F are charged or discharged, resulting in a stretch-out of the C-V curve. A theoretical C-V curve in the absence of interface states is calculated, which requires accurate knowledge of the semiconductor doping density as a function of position from the oxide/semiconductor interface. D_{IT} is then obtained by comparing the experimental C-V characteristic to theory. Since the analysis requires computing the slope of the semiconductor potential versus capacitance curve it is advantageous to increase the number of measurement points.

The interface state density for the same device used for the hi-low analysis was also obtained via Terman analysis. Results from a 1 MHz C-V characteristic at 500K in nitrogen is shown with the + symbols in Figure 4. The 1 MHz C-V curve was taken at a sweep rate of 0.08 V/s with 20 mV steps, resulting in data that overlays that in Figure 3. The doping density used to calculate the theoretical C-V curve was obtained via $1/C^2$ analysis of the C-V curves in depletion [16]. This allows us to account for variations in the epitaxial layer doping density from device to device. We estimate that the Terman results are valid for 0.55 eV < $E_c - E$ < 1.1 eV based on interface state response times. In this energy range the values for D_{IT} obtained from the Terman and hi-low analysis agree to within a factor of three.

The functional form of energy versus D_{IT} that we observe is an artifact of the Terman technique. Using n-type Si based MIS devices Rosencher & Bois determined D_{IT} via deep level transient spectroscopy (DLTS) and 1 MHz Terman techniques [21]. A flat energy independent continuum was obtained using DLTS. Using the interface state density from the DLTS data and known sample parameters they calculated a Terman spectrum, the simulated and experimental spectra agree with each other. Both spectra show a sharp increase in D_{IT} near the conduction band, followed by a minimum then a maximum as the energy is swept towards the valence band. We observe the same functional form in our Terman measurements of SiC based MIS capacitors. Hi-low analysis is a significantly more accurate method of determining the energy dependence of D_{IT} than the Terman technique. However, in SiC devices at high temperature, where hi-low analysis is not possible due to finite gate leakage currents, Terman analysis allows us to estimate the interface state density to within an order of magnitude. An alternative method for determining D_{IT} at high temperatures is conductance-voltage spectroscopy, however high-frequency C-V has the advantage that the same measurement can be directly used to determine sensor response.

Simulated exhaust environments

In order to investigate the mechanisms responsible for the response of $Pt/SiO_2/SiC$ capacitors to hydrogen containing species we have measured the high-frequency C-V characteristics of the device in reducing and oxidizing environments at 800K as shown in Figure 1. The gas ambients consist

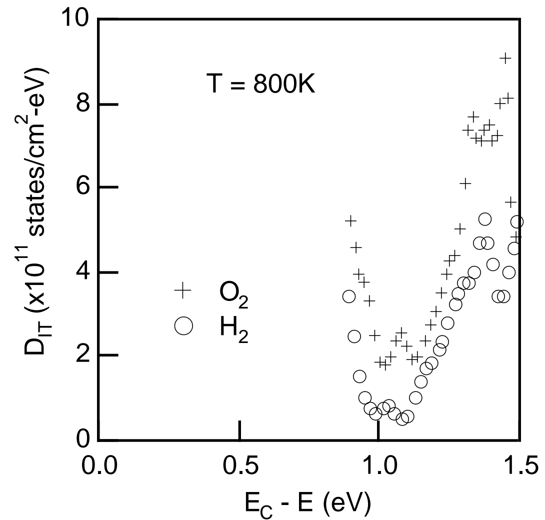

Figure 5. Interface state density at 800K in 1% oxygen and 10% hydrogen ambients (balance gas is nitrogen) obtained from Terman analysis of the data in Figure 1.

of 10% hydrogen and 1% oxygen in nitrogen. We observe two effects. Hydrogen exposure results in a shift of the device flat band voltage to more negative potentials than those observed in oxygen. The transition from accumulation to inversion is sharp in hydrogen, whereas in oxygen the transition is broadened indicating the creation of a large number of interface states. We interpret these results as arising from two separate phenomena. First there is the chemically induced shift in metal/semiconductor workfunction difference (Φ_{MS}). This is the "classic" sensor response as observed in Si based catalytic gate hydrogen sensors at T < 500K [10]. Secondly there is the reversible passivation by hydrogen and creation by oxygen of charged states at the SiO_2/SiC interface. We have confirmed the reversibility of the creation/passivation of these states by repeatedly cycling the $Pt/SiO_2/SiC$ capacitor between hydrogen and oxygen at 800K and measuring the 1 MHz C-V characteristic following each gas change.

To obtain a quantitative measure of the effect of reducing and oxidizing environments on D_{IT} the Terman technique was used to analyze the data in Figure 1. Figure 5 shows that in the energy range 0.9 eV < $E_c - E$ < 1.5 eV the interface state density is a factor of 2 to 3 higher in oxygen than hydrogen. Note the energy range where Terman analysis is valid ($0.30 < C/C_{ox} < 0.46$) lies between gate voltages of $-0.70 \text{ V} < V_g < +0.70$ V for oxygen, whereas in hydrogen the corresponding range is between $-1.3 \text{ V} < V_g < -0.1$ V. Aside from a 0.8 V lateral shift the two C-V curves in Figure 1 are almost identical for these gate biases. This would imply a similar interface state density for the two environments, as observed.

We conclude therefore that at 800K cycling from an oxidizing to reducing ambient causes (i) a negative 0.8 V lateral shift in the C-V characteristic due to the chemically induced change in Φ_{MS} and (ii) a decrease by a factor of 2 to 3

in the interface state density around midgap. The situation near the conduction band edge is quite different. The experimentally measured C-V curve in hydrogen is close to the ideal curve as calculated for a $Pt/SiO_2/SiC$ capacitor free of any interface states in the energy range $E_c - E < 0.9$ eV. In the presence of oxygen, on the other hand, there is a significant broadening of the C-V curve indicating at least an order of magnitude increase in D_{IT}. These states can follow the slow DC bias sweep (0.1 V/s) so their response time at 800K is quite slow, $\tau > 700$ ms. This is a surprising result since these states lie within 1 eV of the conduction band edge. Unfortunately, in this energy range we cannot use Terman analysis to quantify the magnitude of the increase in D_{IT}.

Effect of interface states on gas sensing

To operate the $Pt/SiO_2/SiC$ capacitor as a sensor the device is held at constant capacitance while modulating the gas composition. The gate bias required to maintain the capacitance is the sensor signal. The effect of interface states on the device response clearly depends on the capacitance set point. In the upper portion of the C-V curve slow interface states within 1 eV of the conduction band edge have a large influence on the device in an oxygenated environment. In the lower portion of the C-V characteristic interface states near the SiC midgap have a much smaller effect, factor of 2 to 3, on the C-V characteristic.

The sensor response in the lower portion of the C-V curve, $C/C_{ox} < 0.45$, is dominated by chemically induced changes in the metal/oxide workfunction difference. A –0.8 V signal is obtained in cycling from oxygen to hydrogen and the effect of interface states, located near midgap, is secondary. Although the magnitude of the sensor signal is smaller in the lower portion of the C-V curve it may be more stable to repeated cycling due to the small D_{IT} contribution. In the upper portion of the C-V curve, $C/C_{ox} > 0.45$, two mechanisms, Φ_{MS} and D_{IT}, affect the sensor response. Although the magnitude of the sensor signal is larger in the upper portion of the C-V curve we anticipate that the sensor response to oxidizing environments will be slow, since $\tau >$ 700 ms. These results indicate that the optimum bias point with respect to reliability and time response, for $Pt/SiO_2/SiC$ capacitors operating as hydrogen sensors is in the lower half of the C-V curve.

CONCLUSION

We have shown that the response of $Pt/SiO_2/SiC$ sensors to oxidizing and reducing ambients at 800K is due to two independent phenomena: chemical modification of the metal/oxide workfunction difference and creation/passivation of interface states located primarily in the upper half of the SiC bandgap. Since these MIS capacitance sensors usually operate in constant capacitance mode, the capacitance set point determines both (i) the magnitude of the sensor signal and (ii) the relative contribution of each mechanism towards the sensor response. Under appropriate bias conditions catalytic gate SiC field-effect devices are well suited for hydrogen and oxygen sensing in chemically reactive high temperature environments.

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