

SENSING MECHANISMS OF HIGH TEMPERATURE SILICON CARBIDE FIELD-EFFECT DEVICES

P. Tobias^{a,1}, B. Golding^{a,b}, and R. N. Ghosh^a

ABSTRACT

Metal-insulator-silicon carbide devices have been used for gas sensing in automotive exhausts, because the large band gap of SiC allows high temperature operation up to 1200 K in chemically reactive environments. The sensor response to hydrogen containing species is due to two mechanisms whose effects are difficult to distinguish: the chemical modification of the barrier height at the metal-insulator interface and the creation/passivation of charged states at the insulator-silicon carbide interface. We describe an experimental technique combining *in-situ* photoemission and *in-situ* capacitance-voltage spectroscopy to separate the contribution of each phenomenon. Our experiment elucidates the sensing mechanism of high temperature SiC based gas sensors.

INTRODUCTION

There is a need for gas sensors in the emissions control of automotive exhaust and flue gases, for both real time monitoring and feedback control. Typical operation conditions are high temperature, chemically reactive environments and low or varying oxygen concentrations. To extend the possible operation temperatures from 500 to above 1200 K, silicon carbide (SiC) has been used as the semiconductor instead of silicon, because the band gap of silicon carbide (~ 3 eV) is much larger than the one for silicon (~ 1.1 eV). In addition, SiC is chemically stable, making it well suited for sensing applications in harsh and reactive environments [1].

Until recently, the response of metal-insulator-silicon carbide (MISiC) structures to hydrogen containing species has been ascribed entirely to the chemically induced shift in the metal-insulator work function [2]. This model of sensor response is based on measurements performed on silicon based MIS structures at temperatures below 500 K [3, 4]. We have previously demonstrated that at high temperatures (above 700 K) an additional mechanism, the reversible passivation/creation of charged states near the SiO₂-SiC interface contributes to the hydrogen sensitivity [5]. In this paper, we describe a method to distinguish between the two mechanisms and to study them separately by characterizing the same samples with

in-situ capacitance-voltage curves and *in-situ* photoemission measurements.

MODEL FOR SENSOR RESPONSE

An understanding of the processes at the SiO₂-SiC interface is desirable for any field-effect device with such an interface. Although SiC grows a thermal oxide similar to Si, the interface state density is about a decade larger than in Si, which seriously limits the applicability of SiC structures. Our devices are simple capacitors consisting of circular platinum dots on thermal oxidized silicon carbide, as shown in Fig. 1.

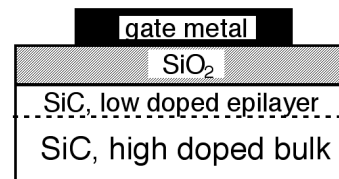


Fig.1: Schematic of the MISiC devices (not to scale). The gate metal is deposited on a thermally oxidized SiC substrate with dot diameters from 200 to 1000 nm. The oxide is about 43 nm thick.

In Fig. 2, we show the C-V curves of an n-type MISiC capacitor [6]. As the voltage is swept from positive to negative bias in a stepwise manner, the silicon carbide near the interface is depleted of majority carriers, and the depleted region increases in thickness. The total capacitance decreases, because it includes the capacitance of the depleted region in series with the oxide capacitance.

To explain how the C-V curves are modified by the presence of hydrogen or oxygen, we show in Fig. 3 a schematic band diagram of our MISiC capacitors biased under flatband conditions. At this bias the bands in the semiconductor are constant with respect to position. The reference energy for electrons in our devices is taken to be the silicon carbide Fermi level, E_F . The applied voltage, V_{FB} , is the difference between the reference energy and the Fermi level in the platinum divided by the electronic charge, q . The energy difference between the Fermi level in the platinum and the conduction band in the insulator is

^a Center for Sensor Materials, BPS, Michigan State University, East Lansing, MI 48824-2320

¹ corresponding author: tobias@pa.msu.edu

^b Department of Physics and Astronomy, BPS, Michigan State University, East Lansing, MI 48824-2320

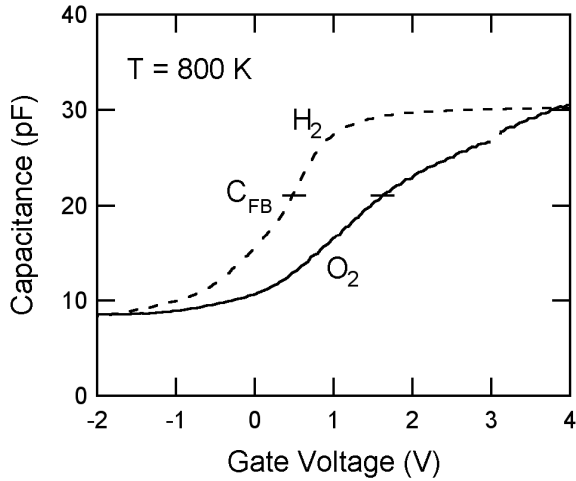


Fig.2: High frequency (1 MHz) capacitance of a sample with a gate area of $3.8 \times 10^{-8} \text{ m}^2$ and an oxide thickness of 43 nm, measured in two gas environments, 10% H₂ in N₂ and 1% O₂ in N₂. The gate voltage is swept from positive to negative voltages at 0.08 V/s. Flatband occurs at $\sim 21 \text{ pF}$ (C_{FB}).

called E . The energy difference, F , between E_F and the insulator conduction band is assumed to be independent of gas exposure.

In hydrogen, Fig. 3 (a), the interface state density at the silicon carbide-insulator interface is essentially zero, to within our experimental uncertainty, whereas in oxygen it is measurable [6, 7]. It is small at midgap and increases towards the conduction band edge. During oxygen exposure the negatively charged interface states, shown in Fig. 3(b), are compensated by positive charge in the metal. This leads to an electric field in the insulator during oxygen exposure, even at flatband conditions in the silicon carbide, and a resulting voltage drop, U . From the band

diagram we deduce, with positive voltages pointing downwards:

$$qV_{FB} = F + (qU) E \quad (1)$$

The voltage drop across the insulator, U , depends on the density per unit area of accessible defects, n , at the insulator- silicon carbide interface below and within kT of E_F . It can be expressed in terms of the insulator thickness, t , the dielectric constant of the insulator, ϵ , and q :

$$U = nqt / \epsilon \quad (2)$$

When the gas environment of the device is changed from hydrogen to oxygen, the resulting change, ΔV_{FB} , of V_{FB} can be related to the changes, ΔE and Δn , of E and n , respectively (F is constant).

$$\Delta V_{FB} = \Delta nqt / \epsilon + \Delta E / q \quad (3)$$

As the gas is changed from hydrogen to oxygen it has been shown that E increases [3, 4]. n increases as well because of the creation of charged states at the insulator-silicon carbide interface [6]. With both E and n increasing in oxygen, V_{FB} must also increase, as seen in Fig. 2.

The effect of the change from hydrogen to oxygen on E is independent of the possible band bending in the silicon carbide. Therefore, in Fig. 2, the increase of E in oxygen is the same for all measurement points and would, without interface states, lead to a parallel shift of the C-V curve along the voltage axis. On the other hand, the density of accessible defects, n , is larger when the Fermi level is close to the conduction band (resulting in large capacitance of the MISiC). This leads to the larger increase of the gate voltage in oxygen for higher capacitances, as seen in Fig. 2.

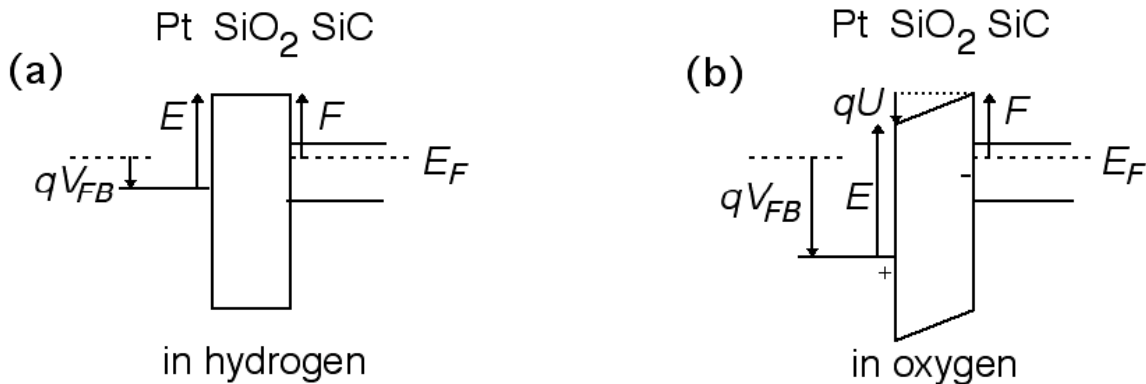


Fig. 3: Band diagram of MISiCs (n-type), at flatband capacitance in (a) hydrogen and in (b) oxygen. The symbols are explained in the text. In oxygen there is an additional potential drop across the insulator due to interface states.

DETERMINATION OF E

To distinguish between the effect of Δn and ΔE , we have set up another experiment to measure ΔE alone, for which the band diagram is shown in Fig. 4. In this experiment, we want to generate a photocurrent, I , over the metal-insulator-barrier that depends on difference of photon energy, hf , and the barrier height, E [3, 8]. The dependence is theoretically quadratic, as shown in Eq. (4) and in Fig. 5, but sometimes it is observed to be closer to cubic [8].

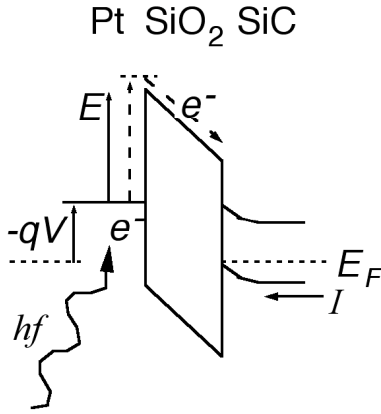


Fig 4: Band diagram of MISiCs (p-type) during the photo emission measurement. Photons with energy, hf , excite electrons in the metal to move to a higher state and then over the metal-insulator barrier. The photocurrent, I , depends on the height of the barrier E .

$$I \propto (hf - E)^2 \quad \text{for } hf > E + 3kT \quad (4)$$

Fig. 5 shows the expected photocurrents in hydrogen and in oxygen when plotted as square roots versus the photon energy. E can be estimated to be about the difference of the platinum work function (~ 5.7 eV) [9], and the electron affinity of the SiO_2 (~ 1 eV) [10]. To investigate the linear region in Fig. 5, the photons must have an energy of more than about 5 eV, which corresponds to wavelengths below 248 nm.

The measured E depends slightly on the bias-voltages, V , by the Schottky effect [11]. V has to be very negative (large arrow upwards in Fig. 4) to collect almost every electron that surmounts the barrier into the semiconductor. A value of E for the field-free case can then be extrapolated from measurements with different V . From measurements with different photon energies, hf , an absolute value of E can be calculated for different gas atmospheres, and therefore also the change ΔE from one gas to another. For a sample, on which both the C-V curve and the photocurrents are measured, Eqs. (3) and (4) allow us to determine the two gas induced changes Δn and ΔE .

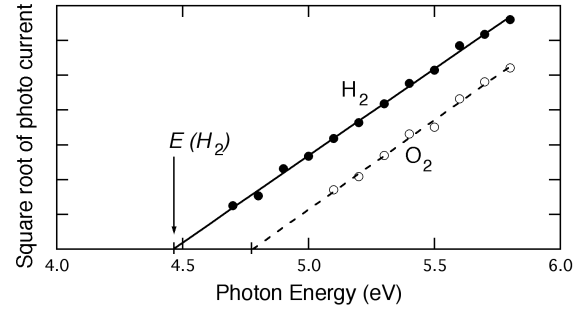


Fig. 5: Simulation of expected results. The absolute metal-insulator barrier height, E , in different gas atmospheres will be determined by plotting a linearized function of the photo versus the photon energies.

SAMPLE PREPARATION

We prepare our samples, see Fig. 1, from SiC wafers [12] with a high doped bulk and a low doped epi-layer on the Si-face. The oxide is grown in dry or wet oxygen, followed by a wet anneal at 1220 K. Metal dots are deposited on the front side of the samples through a shadow mask either by sputtering or by e-beam evaporation at a temperature of 420 K. The metal is Pt, 15 to 100 nm, or 100 nm Pt on 2 nm Ti. More details can be found in [7].

For the photoemission measurement, Fig. 4, it is necessary to excite electrons to a high energy state near the metal-insulator interface, for which a thin metal gate is preferable. The extinction coefficient, k , for Pt at 5 eV is about 1.85 [13], leading to penetration depth of about 24 nm. On the other hand, thin metal films rupture more easily at higher temperature, which leads to isolated metal islands. We have chosen to deposit Pt in thickness of 15-20 nm (which makes them slightly transparent in the visible).

The light will also create electron-hole pairs in the silicon carbide, because the photon energy (~ 5 eV) is much larger than the band gap (3 eV). To minimize the current through this process, we must avoid storing minority carriers at the insulator-semiconductor interface. The gate metal, on the other hand, must be biased negative to enable collection of the injected electrons by the semiconductor. The use of p-type silicon carbide capacitors biased in accumulation achieves these objectives.

The samples are attached on thin alumina headers with gold pads with conducting paste that serves also as the capacitor back contact. Three small resistive platinum heaters on the back of the headers can heat the samples up to 850 K. The MISiCs are contacted by bonding 1 mil gold wire from the gold pads on the alumina headers to the MISiC gates at 620 K. Before photoemission measurements we characterize MISiCs at temperatures from 300 to 900 K in different gases by C-V curves and by sensor measurements at fixed capacitance level [5].

MEASUREMENT SET-UP

The samples are mounted in an UV transparent cell, see Fig. 6, that allows us to heat the samples to temperatures up to 900 K in any chosen gas atmosphere. The device temperature is measured with a thin thermocouple, type K that is fixed at the border of the sample (not shown).

For the photo measurements, the sample is illuminated with UV light in a spectrometer with wavelengths down to 215 nm. The UV light is partly absorbed and excites electrons in the platinum to higher states. Those electrons that cross the metal-insulator barrier contribute to the photocurrent that is measured with a current preamplifier. Another part of the UV light is reflected towards a photo multiplier that can detect changes in the reflectivity of the film.

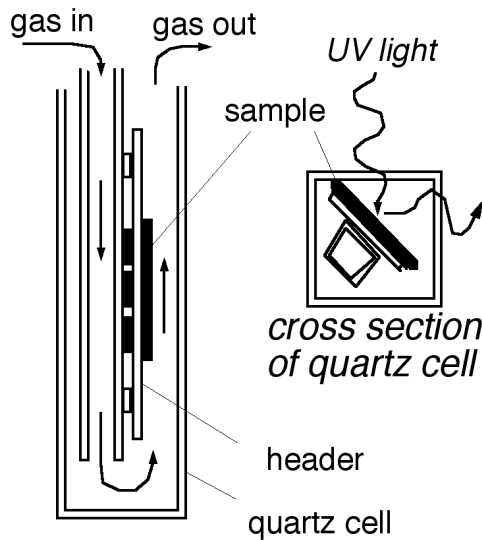


Fig. 6: Schematic sketch of the set up for photoemission measurements with heated devices in a UV transparent gas-flow cell. The sample is mounted onto an alumina header with three backside resistive heaters. Not shown are the electrical leads for heating and for current measurements during UV illumination.

CONCLUSIONS

In summary, we have presented a combination of photocurrent and capacitance-voltage measurements to quantitatively characterize the effects of the two sensing mechanisms in a metal-insulator-silicon carbide field-effect sensor up to 600 °C. The method could also be used in on other MiSiC structures, e.g. to investigate *in-situ* the annealing of interface states by various gases. A

through understanding of the competing phenomena responsible for the electronic and chemical properties of MiSiC structures will enable the design of more stable and reliable SiC based high temperature sensors and electronics.

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