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High-temperature Thin-catalytic Gate Devices for Combustion Emissions Control

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4H- and 6H-SiC Schottky diodes responding down to 5 ppm of NO and NO₂ gases at temperatures up to 450°C were fabricated. Upon exposure to gas, the forward current of the devices changes due to variations in the Schottky barrier height. For NO gas, the response follows a simple Langmuir adsorption model. Device parameters were evaluated from linear conductance/current versus conductance plots, with improved accuracy. The linearity of these plots is an indication that the devices are not being affected by interfacial oxide layers or pinning of the Fermi level. 4H-SiC devices showed slightly superior stability and sensitivity for this application.

1 Introduction

The Nitrogen oxides (NO_x) are produced from the combustion processes, which are the typical air pollutants. NO_x combines with water in the atmosphere and form nitrous acid and nitric acid, which are one of the factors that cause the acid rain. Hence, detection and emission control of toxic NO_x gases, consisting of NO and NO₂, is of great importance [1]. SiC-based sensors that can be used at high temperatures and corrosive atmospheres have been under development for that purpose. Use of catalytic metal gate SiC devices as gas sensors has been extensively investigated by several groups [2-5].

In this work, we report on the development of SiC-based Schottky diodes for detection and monitoring of contaminating gases, specially NO, NO₂ and hydrocarbons for petroleum and automobile industry, operating at high temperatures. Here, we will extend our previous work [7] by the inclusion of additional results in 4H-SiC diodes, response to NO₂ gas and brief discussions of fabrication parameters, response mechanisms and possible directions for future research.

2 Experimental Details

Successful devices described in the literature have been fabricated on heavily doped substrates with an moderately doped epitaxial layer. The heavily doped substrate provides a better ohmic contact and lower series resistance. The epitaxial layer provides a better surface quality and better control of doping concentration. In this work, we also used non-epitaxial wafers to investigate the possibility of fabricating these devices at lower costs. We used n-type, non-epitaxial

6H-SiC, Si face, SiC wafer provided by Nippon Steel Company as well as 4H- and 6H-SiC wafers from Cree Research with 10 μm thick homo-epitaxial layer grown on the Si face. For the epitaxial diodes, bulk and epilayer were n-type; epilayer donor concentration was $1.7 \times 10^{16} \text{ cm}^{-3}$ for 6H-SiC and $1 \times 10^{15} \text{ cm}^{-3}$ for 4H-SiC.

The wafers were ultrasonically cleaned in 5-min steps in acetone, methanol, semico-clean-23 and 46% HF with a 2-min rinse in DI-water between each step. Ni was thermally evaporated to form an ohmic back contact on the C face and vacuum-annealed at 850°C for 2 min. Finally, thin Pt gate (20 nm to 40 nm thick) was deposited by sputtering in Ar gas on the Si face (100) through a metal mask to form circular gate electrodes with a diameter of 1 mm.

The gas response and electrical characteristics of the devices were recorded by an automatic data acquisition system while gas flow alternated between NO or NO₂ diluted in synthetic air (O₂: 20%, N₂: 80%) and synthetic air, controlled by a gas mixing station (AERA Japan Ltd., SG-7S1) with a multi-port valve. The samples were fixed onto a platinum plate by mechanical pressure inside a quartz tube of a temperature controlled furnace, connected close to the gas mixing station in order to reduce the time lag after gas switching. The time lag was within 5 to 10 seconds. I x V (current versus voltage) measurements were taken by means of Pt wires connected to the plate and to a Pt probe pressing the gate.

3 Results and Discussion

At high temperatures, the saturation current of the Schottky diodes increases and the effect of series resistance is

more important, even at low voltages, especially for the non-epitaxial diodes. It is necessary to take this fact into consideration when monitoring the forward characteristics to detect the effect of gas, either in constant current or constant voltage mode. This is illustrated in Fig. 1. The curves were simulated by means of the equation below, either including series resistance or not. They show the effect of a 0.1 eV decrease in barrier height on I x V characteristics.

$$J = J_{sat} \left[\exp \left(\frac{q(V - Jr_{on})}{nkT} \right) - 1 \right] = A^* T^2 \exp \left(\frac{-q\phi_b}{kT} \right) \left[\exp \left(\frac{q(V - Jr_{on})}{nkT} \right) - 1 \right]$$

In principle, the effect of series resistance might be alleviated by monitoring the current of the diodes in reverse bias or by monitoring their depletion capacitance. We chose to monitor the gas response using forward bias, since reverse currents are more likely to be associated with imperfectly understood mechanisms, such as leakage and generation-recombination currents, thus bearing unclear relationship with the detection principle of catalytic gate gas sensors (barrier height changes). To monitor changes in the depletion capacitance is another possibility, although series resistance also affects the measurement of capacitance. The effect of series resistance on capacitance is less important at lower frequencies.

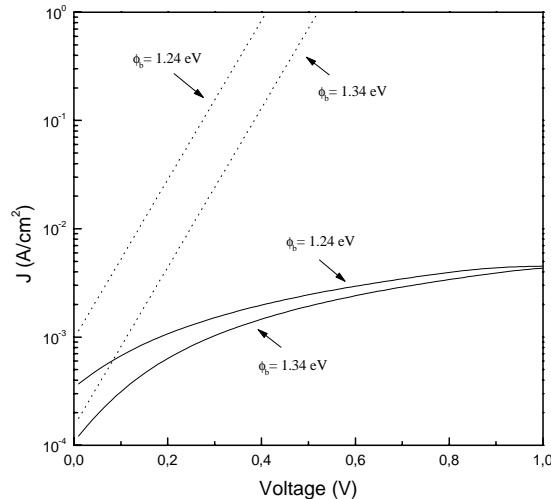


Figure 1. Plot of the forward current density for an ideal SiC Schottky diode (dotted line) and the same diode with a series resistance of $42 \Omega \cdot \text{cm}^2$ at 350°C showing the effect of barrier height changes.

In our work, we have been using an improved technique for the analysis of barrier height changes from I x V characteristics [6][7]. As shown in Fig.1, when the effect of series resistance becomes important, the calculation of barrier height from conventional I x V plot becomes unreliable. A conductance divided by current (G/I) versus conductance (G) plot can be used to analyze the device characteristics. If the G/I x G plot is linear, one is assured that the series resistance (R_s), saturation current (I_{sat}) and ideality factor

(n) of the device are voltage independent, and therefore the usual theory can be applied to the device. We have been using this method to calculate the series resistance, ideality factor and barrier height changes with improved accuracy.

The response characteristics of the devices are summarized in Figs.2-5. In this paper, we are going to show results obtained with epitaxial diodes only. The response of non-epitaxial diodes is similar, showing that they are, in principle, responsive to gas injection. However, barrier height changes tend to become difficult to detect due to their increased resistance. Fig. 2 shows typical I x V characteristics up to 450°C . The inset graph in Fig. 2 depicts the repeatability of the response at 40 ppm and 400°C , obtained by measuring the current at a fixed forward bias of 0.5 V. From Figs. 1 and 2, we see that, upon exposure to NO gas, the I x V characteristics shift reversibly to increased levels. It was possible to detect current variations for NO concentrations ranging from 50 ppm down to 5 ppm.

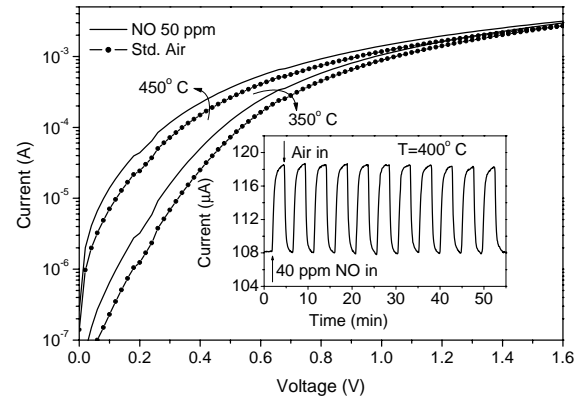


Figure 2. Current-voltage characteristics at elevated temperatures up to 450°C in air (dotted line) and in 50 ppm of NO (solid line) for a thin-Pt/4H-SiC Schottky diode. The inset graph shows current values at a fixed voltage of 0.5 V and temperature equal to 400°C during repeated pulses of 40 ppm of NO.

Figure 3 shows typical relative device current variations as a function of time after pulses of different gas concentrations for a 6H-SiC device. The graph shows the relative current variation when the atmosphere is changed between synthetic air and NO. ΔI is the difference between the current during gas test ($I(t)$) and the reference current (I_0), which is the value measured in synthetic air, just before the beginning of the test ($\Delta I = I(t) - I_0$).

It is important to note that response time and recovery time do not depend on gas concentration. When the data in Fig. 3 is replotted using a common time origin (time = 0 is set to be the instant of time when the pulse of different gas concentrations is injected), it becomes apparent that the response time and recovery time are almost independent on gas concentration, as shown in Fig. 4. This is further demonstrated in Fig. 5, which shows the normalized gas response using a common time origin. It is apparent that all the curves have approximately the same shape, with some fluctuations due to electrical noise.

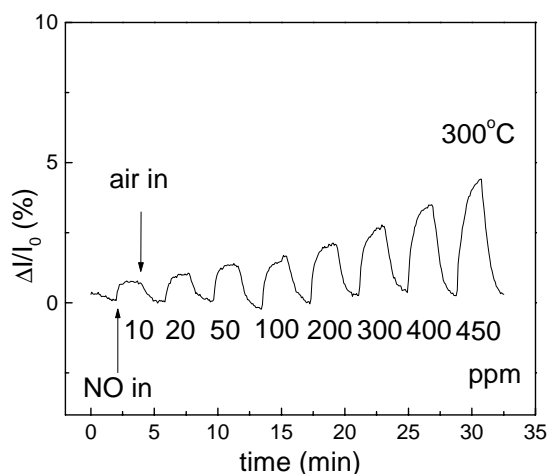


Figure 3. Response of a thin-Pt/6H-SiC Schottky diode to various NO concentrations. Bias fixed at +0.5 V.

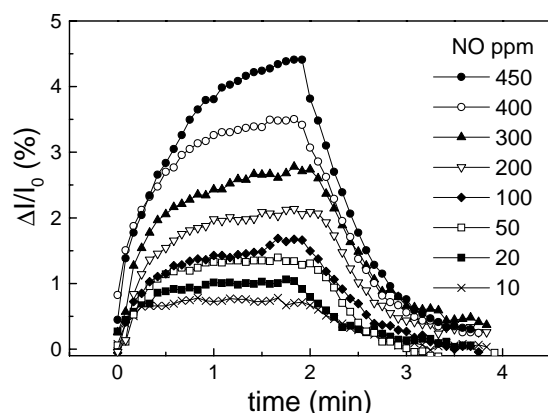


Figure 4. Gas response shown in Fig. 3 replotted using a common time origin. Time equal to zero is set to be the instant when the pulse of gas of different gas concentrations is injected.

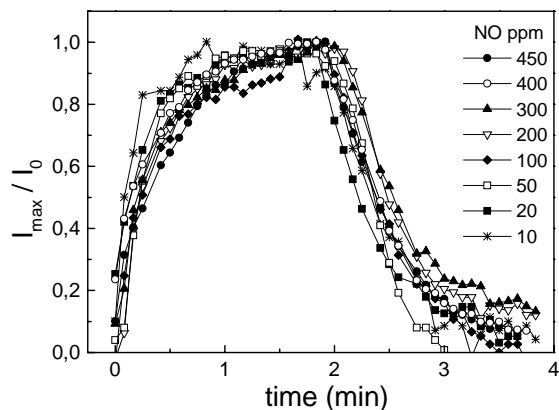


Figure 5. Normalized gas response using a common time origin.

The response to NO is qualitatively the same for both 4H-SiC and 6H-SiC diodes. We have found that relative device current variation for 4H-SiC diode is slightly stronger than for 6H-SiC ones. We also observed that 4H-SiC devices above 400°C are more stable than 6H-SiC devices. The response depends on temperature and tends to be stronger at higher temperatures. Barrier height reduction was found to be approximately 3% for 4H-SiC and 1.8% for 6H-SiC diodes for exposure to 50 ppm of NO at 400°C. The reason for this difference is not clear. It may be related with substrate quality, barrier height or interface states, for example.

We have found that a simple Langmuir adsorption model can adequately describe the gas response to NO. We refer the reader to our previous work, where we derive and discuss this model in detail [7]. The Moreover, the linearity of the $G/I \times G$ plot is an indication that the devices are not being affected by interfacial oxide layers or pinning of the Fermi level.

We have been investigating the response of these devices to other gases, such as NO₂. Fig. 6 shows a typical response of a device to NO₂. For NO₂, exposure to gas makes the barrier height to increase, whereas for NO the barrier height tends to decrease. Our experiments show that the response to NO₂ is more complex than for NO and further investigation is necessary to establish the correct model. It is possible that the adsorption sites for NO₂ have a different polarization direction in comparison with NO adsorption sites.

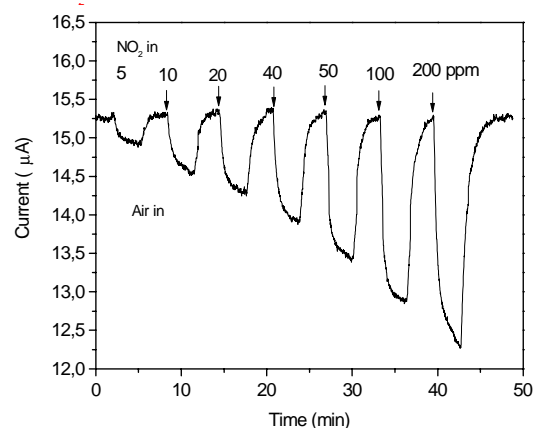


Figure 6. Response of a thin-Pt/6H-SiC Schottky diode to various NO₂ concentrations, at 300°C.

It is interesting to note that similar differences (barrier height increase or decrease depending on gas) were also found in experiments using Si diodes [8]. The sensing properties of thin catalytic metal gate devices seem to depend in a complex way on the thickness, the structure of the film and the polarization phenomena. Various effects may occur, such as reversal of voltage shifts and enhancement or decrease of gas sensitivity after gas exposure. In previous experiments in our group [8] and other groups [9], it has been observed a reversal and enhancement of voltage shift due to NO₂ flow when the devices were submitted to a treatment with NH₃. One reason for this behaviour might be the

presence of two different kinds of NO₂ adsorption/reactions on thin-Pt gates: one, which causes a positive voltage shift and another, which causes a negative voltage shift and is activated by the ammonia.

We are currently investigating the response to other gases as well as different fabrication methods of the thin-Pt gate, including laser ablation and mixtures with sensitive oxides.

4 Conclusions

We developed SiC-based NO and NO₂ sensitive devices operating at high temperatures. Detection of NO and NO₂ down to 5 ppm at temperatures up to 450 °C was demonstrated. The response to NO follows a simple Langmuir adsorption model. The response time and recovery time do not depend on gas concentration. 4H-SiC devices have slightly superior stability and sensitivity for this application.

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