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# SiC-BASED SCHOTTKY DIODE GAS SENSORS

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**Abstract**

Silicon carbide based Schottky diode gas sensors are being developed for high temperature applications such as emission measurements. Two different types of gas sensitive diodes will be discussed in this paper. By varying the structure of the diode, one can affect the diode stability as well as the diode sensitivity to various gases. It is concluded that the ability of SiC to operate as a high temperature semiconductor significantly enhances the versatility of the Schottky diode gas sensing structure and will potentially allow the fabrication of a SiC-based gas sensor array for versatile high temperature gas sensing applications.

## 1.0 Introduction

The sensitive detection of hydrogen ($H_2$), hydrocarbons ($C_xH_y$), and nitrogen oxides ($NO_x$) is important for emission monitoring, chemical process control, and other high temperature applications. The development of SiC as a high temperature semiconductor allows the fabrication of sensors which function in conditions where silicon (Si) based technology is inoperable. This allows the development of gas sensitive electronic structures such as Schottky diodes which can operate at temperatures high enough to allow the detection of $C_xH_y$ or $NO_x$. The advantage of a Schottky diode structure in gas sensing applications is its high sensitivity. This is especially useful in applications such as emission monitoring where the gas concentrations to be measured are low.

Linkoping University has investigated a gas sensitive Schottky diode structure composed of Pt on 15 nm of $TaSi_x$ on a native oxide of $SiO_2$ on SiC. This sensor has a very quick response time to $C_xH_y$ and is stable for extended periods at high temperatures. The magnitude of the diode signal changes by less than an order of magnitude as the ambient is changed from 2% oxygen in argon to 1% propane in argon at 550°C [1-2].

A simple and highly sensitive Schottky diode structure is a catalytic metal directly deposited on a SiC semiconductor (MS). Previously, we have investigated Pd directly deposited on SiC (Pd/SiC) [3]. This Schottky diode is very sensitive to $H_2$ and $C_xH_y$: changes of more than a factor of a 1000 in the forward current have been observed at 300°C in response to 360 ppm of $H_2$, propylene, and ethylene. However, the Pd/SiC diode response drifts if operated at high temperatures for extended periods of time due to, in part, reactions between the Pd and SiC.

A major thrust of the development effort at NASA Lewis Research Center (LeRC) and Case Western Reserve University (CWRU) is the stabilization of the SiC-based sensor structure for long-term, high temperature operation while maintaining high sensitivity [3-4]. Of equal importance is the ability to selectively differentiate between various gases in a mixture. This can be accomplished by using an array of high temperature gas sensors [5] composed of both SiC-based sensors and other sensing materials and platforms. The end result would be, in effect, a high temperature electronic nose for harsh environments. The realization of this objective entails the fabrication of a variety of SiC-based gas sensors with varying sensitivities to different gases.

The purpose of this paper is to discuss the SiC-based gas sensing Schottky diode structures under development at NASA LeRC and CWRU. Two types of structures will be discussed: 1) A catalytic alloy, palladium chrome (PdCr), deposited directly on the SiC forming a MS structure and 2) A catalytic metal (Pd) deposited on a chemically reactive insulator tin oxide ($SnO_2$) adherent on the SiC forming a metal-reactive insulator-semiconductor structure (MRIS). It is concluded that both structures show improved stability over the Pd/SiC diode while maintaining high sensitivity.

## 2.0 Device Fabrication and Testing

The characterization of two types of samples will be discussed in this paper. The first type is a PdCr/SiC Schottky diode while the second is a sample containing both Pd/SiC and Pd/SnO2/SiC Schottky diodes on the same chip. In both samples, a 4-5 $\mu$m thick alpha-SiC epilayer was grown by chemical vapor deposition on a commercially available alpha-SiC substrate. A backside contact was achieved by sputtering aluminum onto the bottom of the wafer.

The PdCr/SiC diodes were formed by co-sputtering with a Pd target and a separate Cr target approximately 400 angstroms (Å) of PdCr metal onto the as-grown SiC epilayer surface and patterning by a lift-off technique to form circular PdCr Schottky patterns of diameter 200 $\mu$m. The Pd/SiC and Pd/$SnO_2$/SiC Schottky diodes were formed in the following manner: a thin layer (approx. 50 Å) of $SnO_2$ was sputter deposited onto half of the substrate while the other half of the substrate was masked during this deposition and was left as-grown. Circular Pd contacts were formed by sputter deposition and lift-off as done with the PdCr/SiC diodes. Thus, one side of the sample formed Pd/$SnO_2$/SiC Schottky diodes while the other side of the sample formed Pd/SiC Schottky diodes; in effect, this is a small sensor "array" composed of two types of diode elements.

The gas sensor testing facility and sample connections have been described elsewhere [3]. The sample rested on the hot stage whose temperature was controlled from room temperature to 425°C. Current-time (I-t) measurements were taken to characterize the diode response as a function of time during exposure to a variety of gases, and current-voltage (I-V) measurements were taken to characterize the diodes electronics properties in given environment. The forward voltage at which the current was measured was chosen to maximize the diode response to the hydrogen-bearing gas and to minimize series resistance effects.

## 3.0 Results and Discussion

### 3.1 PdCr MS Schottky Diode

The advantages of PdCr as a high temperature alloy have been explored extensively in strain gage applications [6]. It is a stable high temperature material which is able to provide static strain measurements at temperature up to 1100°C. However, its use in a gas-sensing SiC-based structure depends on not only its inherent stability but also such factors as the alloy's reactivity to SiC and the catalytic interactions of PdCr alloy with the gases to be measured. The sensitivity and stability of the PdCr/SiC diode were characterized in the following manner.

An as-deposited diode was first operated at 100°C to establish the baseline electronic properties. Current-time measurements at 0.7 V were taken as the sensor was exposed to 20 minutes of air, 20 minutes in nitrogen ($N_2$), 20 minutes of 120 ppm $H_2$ in $N_2$ ($N_2$/$H_2$ mix), 10 minutes of $N_2$, and then

10 minutes of air. After the baseline condition was established, the diode was heat treated at 425°C in air for periods of at least 13 hours. The diode temperature was then decreased to 100°C and the diode was then characterized in the same manner used to establish the baseline. This cycle of heating followed by diode characterization at 100°C was repeated until the total time of heating at 425°C was 250 hours.

Figures 1-2 demonstrate that PdCr/SiC is a viable diode structure for high temperature gas sensing applications with improved stability compared to Pd/SiC [3]. Fig. 1 shows the current at 0.7 V at 100°C in air and in the $N_2/H_2$ mix as a function of heating time. While the air baseline current drifts lower with heating time, the current in the $N_2/H_2$ mix is relatively stable after the initial heating period of 40 hours. This is demonstrated in Fig. 2 where I-t is shown for various gas mixtures: the sensor baseline in air is much lower after 250 hours of heating than at 40 hours, but the sensor current in the $N_2/H_2$ mix is the same within a factor of 3. Thus, the diode's sensitivity to $H_2$ is nearly two orders of magnitude larger at this voltage after 250 hours of heating with the corresponding magnitude of the signal in $H_2$ being nearly constant after 40 hours.

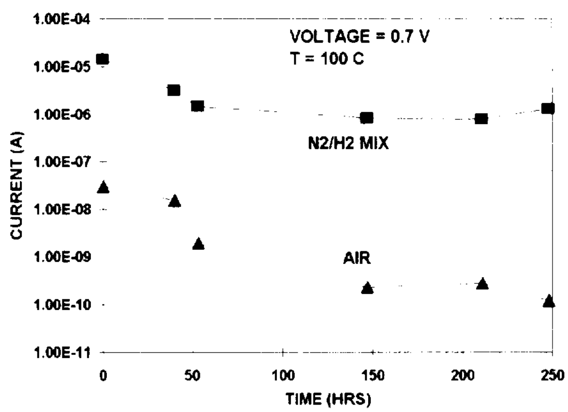


Fig. 1. The forward current at 100°C vs heating time at 425°C in air (▲) and in 120 ppm $H_2$ in $N_2$ (■).

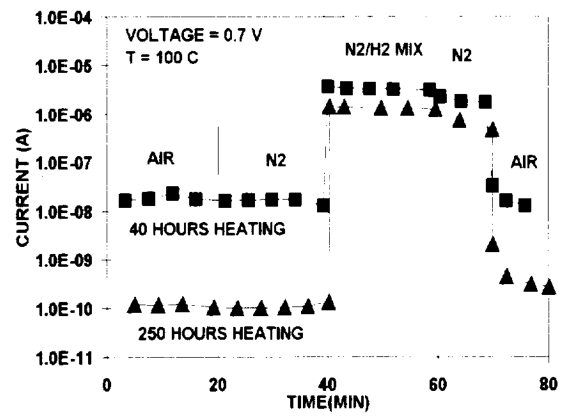


Fig. 2. The forward current vs time at 100°C after 40 hours (■) and 250 hours (▲) heating at 425°C in air.

### 3.2 Metal-Reactive Insulator SiC Schottky Diodes

A wide variety of materials, e.g. metal oxides such as $SnO_2$, are sensitive to $C_xH_y$ and $NO_x$ at high temperatures. These materials could be incorporated as a sensitive component into MIS structures and, unlike silicon, SiC-based devices can be operated at high enough temperatures for these materials to be reactive to gases such as $C_xH_y$ and $NO_x$ [3]. This results in a new type of gas sensitive structure: a metal-reactive insulator-semiconductor structure (MRIS). The advantages of this type of SiC-based structure include 1) increased sensor sensitivity since the diode responds to gas reactions with not only the catalytic metal but with the reactive insulator as well. 2) improved sensor stability since the gas reactive insulator can act as a barrier layer between the metal and SiC potentially stabilizing the sensor's structure. 3) the ability to vary sensor selectivity by varying the reactive insulator element. This paper demonstrates the use of this type of MRIS sensor.

Operation of a Pd/$SnO_2$/SiC sensor and comparison of this sensor with a Pd/SiC sensor on the same chip is shown in Figures 3-4. Two different carrier gases are used: pure $N_2$ and an air/$N_2$ mixture. The sensors are first exposed to air for 15 minutes, then the carrier gas for 15 minutes, followed by 400 ppm of a hydrogen-bearing gas in the carrier gas, 5 minutes of the carrier gas, and finally 10 minutes in air. The air/$N_2$ carrier gas had a constant oxygen concentration of 10%.

The effect of the thin $SnO_2$ layer is most easily seen in the I-V curves of Fig. 3 for the Pd/$SnO_2$/SiC and Pd/SiC diodes respectively. The I-V curve for the Pd/$SnO_2$/SiC diode in Fig. 3 shows parallel shunt resistance for voltages below 1.0 V, and exponential Schottky behavior above 1.0 V until series resistance effects begin to dominate. The barrier height derived from the exponential portion of the curves suggests that the $SnO_2$ increases the barrier height of the diode. The effect of the 400 ppm $H_2$ in $N_2$ on the I-V curve was to increase the current for a given voltage, with the increase in current in the shunt resistance region being somewhat lower than the increase in the Schottky region. This increase in current (resistance decrease) was also noted when the resistance across just the $SnO_2$ was monitored with probes under the same conditions. Thus, $SnO_2$ affects the response to hydrogen of the diode with higher sensitivity to hydrogen noted in the exponential Schottky-like conduction region. In contrast, the Pd/SiC diode shows two types of I-V behavior: an exponential response in the low voltage regions and a series resistance effects at higher voltages. These results clearly show that the $SnO_2$ changes the sensor's basic electronic behavior and the sensor response to $H_2$.

Fig. 4 shows the response of both the Pd/SiC and the Pd/$SnO_2$/SiC diodes to $H_2$, methane, and propylene that were aged over a several week period at 350°C. The Pd/SiC sensor does not respond to 400 ppm of $H_2$ (Fig. 4) or propylene and methane (not shown) in the air/$N_2$ mixture. However, the Pd/$SnO_2$/SiC sensor responds with increasing signal strength to methane, $H_2$, and propylene. That the Pd/$SnO_2$/SiC sensor response to propylene is stronger than that to $H_2$ is significant; the Pd/SiC response in $N_2$ [3] and in $N_2$/air to propylene and $H_2$ was reversed. Thus, the addition of the $SnO_2$ layer makes possible the detection of gases not detected without the layer. It should be noted that the response of the Pd/SiC sensor degraded over the several week period of 350°C operation while the Pd/$SnO_2$/SiC sensor remained relatively stable.

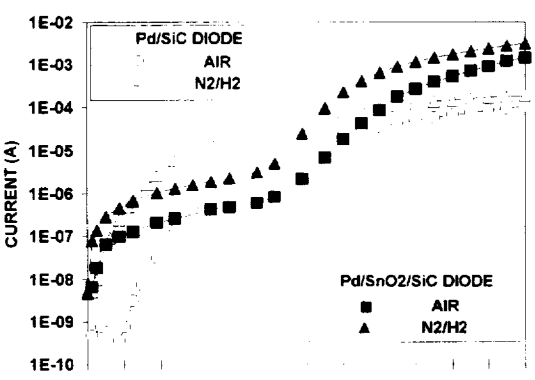


Fig. 3. Current vs voltage at 350°C for a Pd/SiC diode in air (○) and the 400 ppm $N_2$/$H_2$ mix (Δ), and a Pd/$SnO_2$/SiC diode in air (■) and the $N_2$/$H_2$ mix (▲).

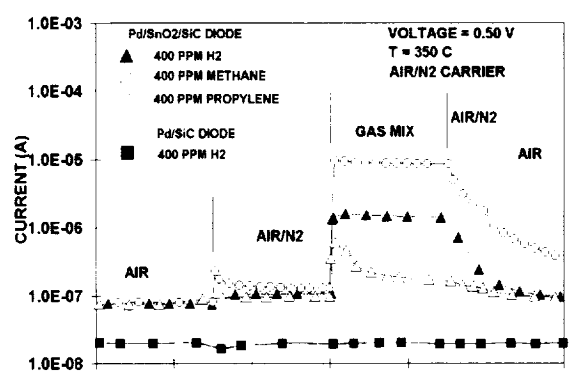


Fig. 4. Current vs time at 350°C for a Pd/SiC diode exposed to 400 ppm $H_2$ (■) and a Pd/$SnO_2$/SiC diode exposed to 400 ppm of $H_2$ (▲), methane (Δ), and propylene (○).

## 4.0 Conclusions and Future Plans

The demonstration of both the PdCr/SiC MS diode and the Pd/$SnO_2$/SiC MRIS diode as stable and sensitive gas sensors shows the versatility of SiC as semiconductor for high temperature gas sensing applications. Future plans include the investigation of other MS and MRIS structures with the eventual goal of forming SiC-based arrays for high temperature gas detection.

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