Improved Sensitivity SiC Hydrogen Sensor

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ABSTRACT

We have produced silicon carbide sensors by two techniques: palladium coating and low energy palladium implantation. The palladium implantation was done at 550°C into the Si face of 6H, n-type SiC at various energies and at various fluences. The sensitivity of each sensor was measured at temperatures between 20°C to 400°C. The response of the SiC sensors produced by Pd implantation has revealed a completely different behavior than the SiC sensors produced by Pd deposition. In the Pd deposited SiC sensors, as well as in the ones reported in the literature [1, 2], the current rises in the presence of hydrogen at room temperature as well as at elevated temperatures. In the case of Pd implanted SiC sensors, the current decreases in the presence of hydrogen whenever the temperature is raised above 100°C [3].

INTRODUCTION

Silicon carbide is intended for use in fabrication of efficient high temperature hydrogen sensors. Traditionally, when a palladium coating is applied on the exposed surface of SiC, the chemical reaction between palladium and hydrogen produces a detectable change in the surface chemical potential. In the past few years, the field of gas sensors based on silicon carbide operating at high temperatures has known a considerably increasing interest among the research teams all over the world, due to their potential applications in hot engine controls for aerospace and automobile applications, as well as process gas monitoring. Because of its outstanding toughness and thermal stability, silicon carbide, a semiconductor material with a wide bandgap and low intrinsic carrier concentration, can potentially operate up to 1000° C.

In addition to the palladium-coated sensors, we have also studied the effects of implanting palladium ions into the Si face of 6H, n-type SiC. Different ion energies and fluences have been studied at an implantation temperature of 550° C. Palladium coated samples were also prepared by electron beam assisted deposition in order to compare their response with the response of the implanted samples. After their preparation, the samples were exposed to hydrogen while monitoring the current flow across the sample (face to face) with respect to time. The temperature monitor design for correcting for current modifications due to temperature fluctuations that we used for the last set of measurements which we reported at the previous MRS meeting was replaced this time by a different setup that controls the uniformity in the temperature of the incoming gases. The response of the implanted samples has revealed a completely different behavior than the samples that have Pd deposited as a surface layer whose response agrees with the similar experiments reported in the literature [1, 2], confirming the results that we already reported previously [3] on samples implanted in slightly different conditions. Our previous report has shown a response at room temperature. However, it could be established in the meantime that this was due to a parasitic injection of carriers from the temperature sensor (this is one of the reasons that stood for its removal from the system).

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EXPERIMENT

For this study we prepared our samples in two ways: by deposition and by ion implantation. The implantation was done in collaboration with Oak Ridge National Laboratory, at 80 keV and 160 keV and fluences between 1×10^{15} and 1.2×10^{16} ions/cm², at 550° C. The current measurements were performed using a Keithley 595 IV/CV meter interfaced with a computer for temperatures near 20, 200, 400° C in a closed gas environment, for applied voltages of ± 1 V on the backside (the opposite side from the one implanted/deposited) of the sample. The current pick-up was realized by the mean of a gold needle used as a probe on the active (implanted/deposited) side of the sample. A schematic drawing of the setup can be seen in figure 1. For this experiment, air was cycled with an H₂-Ar mixture having 4% hydrogen (known as forming gas).

Figure 1. Experimental setup used for testing the sensors (schematic drawing).

RESULTS

A first result, as it can be seen in figure 2a, is that the implanted sensors do not give any dependable response at room temperature. The room temperature reversed response reported in our previous report has been discovered to be due to the parasitic injection of carriers through the thermocouple temperature sensor used in the old setup. On the other hand, the deposited samples show a very clear response (figure 2b, 2c) for both, positive and negative voltage applied. Although the recovering cycle (the exposure to air past the exposure to H₂-Ar mixture) was as long as 10 minutes, for negative voltage this was still not long enough to allow full recovery, while for positive bias it seems to be enough. The delay of about one minute in response is due to the necessary travelling time for gas on the common portion of tubing between the switching valves and experimental chamber (approx. 1 m and a flow rate of 100 mm³/s). The spikes and

sudden steps that can be seen in figure 2a as a new cycle begins are due to vibrational moving of the gold probe on the sample as the operators touches the gas control valves. They couldn't be related to a specific species of gas.

Figure 2a. Implanted Pd, +1V, at room temperature.

Figure 2b. Deposited Pd, -1V, at room temperature.

Figure 2c. Deposited Pd, +1V, at room temperature.

Pictures 3a, 3b, 3c, and 3d show the behavior at 200° C and 400° C. For the deposited sample, even though the response to hydrogen at 200° C is sharper than at room temperature, for negative voltage 10 min. of recovery time is still not enough. Just at 400° C the recovery time drops to about 8 min.

CONCLUSIONS

For the implanted samples, as a general behavior, it could be observed that for the same fluence, the response (defined as $\Delta I/I_{air}$) is greater for lower implantation energies, while for the same implantation energy, the response is better for the lower implantation fluence (see table 1). It seems like the lower the damage induced to the silicon carbide lattice by implantation, the better the response is, although not necessarily faster or slower. That leads to the two possible mechanisms that occur in the presence of hydrogen:

- the hydrogen diffusion inbound;
- the capture of the diffusing hydrogen by the implanted palladium ions, as well as silicon and carbon in the lattice, that would try to saturate with hydrogen their bounds broken during the implantation.

Figure 3a. Pd implanted, $1e15$, 160 keV, -1V.

Figure 3b. Pd implanted, $1e15$, 160 keV, +1V.

Figure 3c. Pd deposited, Si side, -1V.

Figure 3d. Pd deposited, Si side, +1V.

In the case of the sample implanted at 80 keV with 1×10^{15} ions/cm² there is a smaller number of broken Si and C bounds (i. e. smaller number of "docking" points for hydrogen). However, the hydrogen diffuses slower to reach the palladium embedded under the surface of the silicon carbide chip than in the case of more damaged samples (1×10^{15} at 160 keV, and 1.2×10^{16} at 160 keV), so that the two processes seem to compensate each other.

The palladium deposited sensors have a very good response to hydrogen, compared to the implanted ones, even at room temperature. The problem encountered, however, is the perisability of the palladium deposition at elevated temperatures. The time for which the sensor worked properly at 400° C was approximatively 30 hours. This is a serious drawback of this kind of sensor, compared to the ones for which palladium was implanted, whose response after ~30 hours at 400° C had no visible alterations.

Further work will be focused on increasing the sensitivity of the palladium implanted sensors, as well as on improving the stability of the palladium coating at elevated temperatures, for the case of palladium deposited sensors.

Table 1. Response, defined as $\Delta I/I_{\text{air}}$, for three implanted samples and one deposited.

Temperature Sensor	Room temperature		200° C		400° C	
	-1V	+1V	-1V	+1V	-1V	+1V
$1.2 \times 10^{16}/160 \text{ keV}$	N/A	N/A	6×10^{-3}	1.2×10^{-2}	7×10^{-3}	1×10^{-2}
$1 \times 10^{15}/160 \text{ keV}$	N/A	N/A	1×10^{-2}	1.1×10^{-2}	9×10^{-3}	8×10^{-3}
$1 \times 10^{15}/80 \text{ keV}$	N/A	N/A	1.1×10^{-2}	2×10^{-2}	N/A	2×10^{-2}
Pd deposited	.44	3	1	25	200	1.8

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