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Sensing Characteristics of a Novel NH₃-Nitrated Schottky-Diode Hydrogen Sensor

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Abstract – A novel NH₃-nitrated Schottky-diode hydrogen sensor has been successfully fabricated. Measurements have been performed to investigate the sensitivity, stability and response speed of the sensor at different temperatures and hydrogen concentrations. It can respond to hydrogen variation very quickly and can give significant response even at low hydrogen concentration. The studied device exhibits high sensitivity of 350 % at 300 °C when 800 ppm H₂ in N₂ gas is introduced. The sensitivity is 15 times greater than that of the Pt-SiC sensor. The excellent hydrogen-sensing characteristics of this novel sensor make it very suitable for detecting hydrogen leakage in high-temperature environment. The effects of hydrogen adsorption on the barrier height and hydrogen reaction kinetics are also investigated.

I. INTRODUCTION

Hydrogen is a very dangerous gas because it can cause serious explosion if a spark is present. In order to prevent these accidents, hydrogen sensors have become increasingly important in leakage detection for industrial fabrication processes and hydrogen-fueled vehicles, especially at high temperature. Gas sensors based on silicon can operate in environments only below 250°C because of its relatively small band gap (1.12 eV). Compound semiconductors such as SiC, CdS, GaP, etc with wider band gap (about 3 eV) can operate potentially up to 1000°C. Thus, they are very suitable for making hydrogen sensors, which can function in harsh environments such as hot-engine and car exhaust.

A lot of research on hydrogen sensors has been done. Different materials and fabrication methods were used to make the sensors [1-4]. It has been reported that Schottky diodes with palladium (Pd) directly deposited on SiC can sensitively detect hydrogen and hydrocarbon gases. However, after heating of this structure for a long time, there are interfacial reactions between Pd and SiC forming palladium silicides, which cause drift in sensor properties [5].

In order to reduce these interfacial reactions, a gate insulator is placed between Pd and SiC. Several gate insulators such as SnO₂ [6], SiO₂ [7-9] have been used. They are grown in O₂ ambient. Unfortunately, it has been demonstrated that there is still intermixing of materials at the interfaces of the Pd/SiO₂/SiC Schottky sensors after long-duration high-temperature annealing due to poor interfacial diffusion barrier [6]. The sensitivity and stability of a sensor's response depend largely on the gate insulator. The interface between the gate insulator and the substrate can greatly influence the sensor performance. Therefore, the development of high-quality gate insulator for the sensors is a very important issue. In order to simplify the fabrication procedure as well as to prevent the formation of silicides at the Schottky interface, a novel NH₃-nitrated Schottky-diode hydrogen sensor is proposed. This paper will first describe the fabrication procedure of this hydrogen sensor and the measurement methodology. Then, it will investigate the hydrogen sensing properties of the device. Finally, the hydrogen reaction kinetics of the device are studied.

II. EXPERIMENTS

N-type (0001) Si-face 6H-SiC wafer, manufactured by CREE Research, was used in this study. The SiC wafer had a 5-μm epitaxial layer grown on heavily doped substrate. The doping level of the epitaxial layer was $4 \times 10^{15} \text{ cm}^{-3}$. The wafer was cleaned using the conventional RCA method followed by a 20 sec. dipping in 1% hydrofluoric acid to remove the native oxide. When the temperature of the furnace reached 900 °C, the wafer was loaded into the furnace with N₂ inside to prevent wafer from oxidation. Then N₂ gas was closed and NH₃ with a flow rate 0.25 l/min was injected into the furnace to do nitridation for 5 min. This formed a nitrogen-terminated passivation layer on the surface of the SiC wafer. This passivation layer introduced nitrogen to the wafer to help remove dangling bonds and fixed oxide charges. Annealing was then done in-situ at the nitridation temperature in N₂ for 10 min. The purpose of doing annealing was to eliminate strains and defects and make the

quality of the nitride better. Electrodes were then formed by DC-magnetron sputtering at a substrate temperature of 350 °C. The front electrode of 10-nm TaSi_x and 100-nm Pt in the form of dots with diameter of 0.5 μm was deposited on the nitride through a stainless steel mask. The back electrode of 200-nm TaSi_x and 400-nm Pt was formed after etching off the oxide. The sample underwent metal annealing by loading it into the furnace at 650 °C with N₂ flowing inside (1000ml/min) for 30 min. For the purpose of comparison, a control sample without any nitride or oxide layer was also fabricated.

After the fabrication of the hydrogen sensors, their performance was recorded. In order to facilitate taking data, a computer-controlled measurement system was used. This measurement system mainly consisted of two parts: the gas mixing supply system and the parameter-testing system. The sensor was placed in a copper reaction chamber enclosed in a thermostat and the chamber was connected to digital gas flow controllers. Computer programs were used to investigate the characteristics of the hydrogen sensors by controlling the digital gas flow controllers, the thermostat and the HP4145B semiconductor parameter analyzer.

III. RESULTS AND DISCUSSION

Fig.1 shows the I-V curves of the NH₃-nitrided sample measured in air and in different hydrogen concentrations (48 ppm, 238 ppm and 619 ppm) at 25 °C and 300 °C. The I-V curve shifts to the left as temperature increases. At 25 °C, the sensor shows little response upon exposure to different hydrogen concentrations, but the hydrogenation effect becomes more obvious at 300 °C. The I-V curves shift to the left as hydrogen concentration increases. The shift toward a lower voltage is due to the formation of a polarized layer at the electrode-nitride interface. When the hydrogen-containing molecules come to the front electrode, they dissociate at the surface of the electrode and form hydrogen atoms. These hydrogen atoms will diffuse through the electrode in the order of nano- to microseconds to the surface of the passivation layer and form a polarized layer at the electrode-nitride interface [10]. This polarized layer causes a change in the number of mobile carriers in the Schottky sensor and this provides an extra electric field to lower the barrier. In study, reverse bias is not used to characterize the sensor response to different H₂ concentrations because no polarized layer is formed at the bottom electrode-nitride interface under reverse bias. Therefore, not much shift in the I-V curve can be seen with exposure to hydrogen-containing gases.

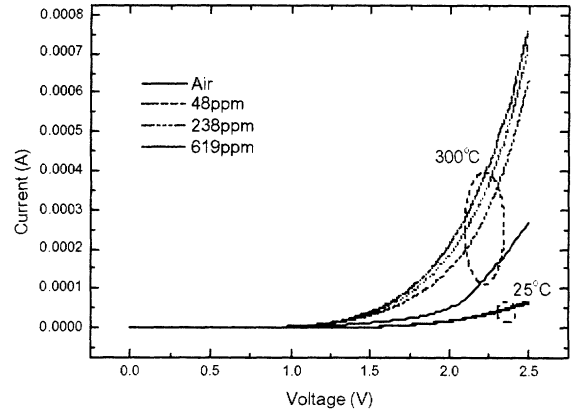


Fig.1 I-V curves of the NH₃-nitrided sample measured in air and in different hydrogen concentrations (48ppm, 238ppm and 619ppm) at 25°C and 300°C.

Based on the thermionic emission conduction mechanism of Schottky diode, for forward bias $V > 3kT/q$, the I-V characteristics of a Schottky diode are given by

$$I = I_o \exp\left(\frac{qV}{nkT}\right) \quad (1)$$

where k is the Boltzmann constant, T the temperature in K, n the ideality factor, and I_o the saturation current defined as

$$I_o = AA^{**} T^2 \exp\left(-\frac{\phi_b}{\phi_T}\right) \quad (2)$$

where A is the junction area, A^{**} the effective Richardson constant, ϕ_b the barrier height of the Schottky diode and $\phi_T = kT/q$. Plot of $\ln I$ vs V (in air and in 800 ppm H₂ in N₂ gas) at 300 °C is shown in Fig.2. The graph shows good linearity, which indicates that the current conduction mechanism of the novel NH₃-nitrided Schottky hydrogen sensor is controlled by the thermionic emission mechanism.

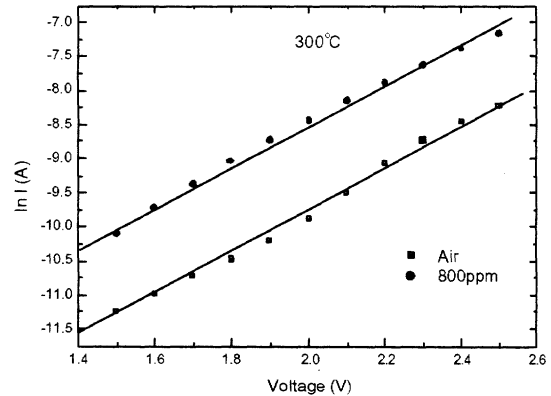


Fig.2 I-V characteristics of the NH₃-nitrided sample at 300 °C in (1) air, and (2) 800 ppm H₂ in N₂.

Presented in Fig.3 is the sensor response of the NH₃-nitrided sample upon alternate exposure to air and 800 ppm H₂ in N₂ at 25 °C and 300 °C. The applied forward current is 1 mA. The sensor can give a larger and more rapid and stable response at higher temperatures. It is because at high temperature, hydrogen molecules have more energy and can decompose faster into hydrogen atoms at the surface of the electrode. More hydrogen atoms can diffuse through the electrode faster and hence give a larger voltage shift and faster response. At 300 °C, the recovery time of the sample is longer than the response time. This shows that time is more needed for hydrogen atoms to diffuse out of the electrode surface and then recombine together to form hydrogen gas.

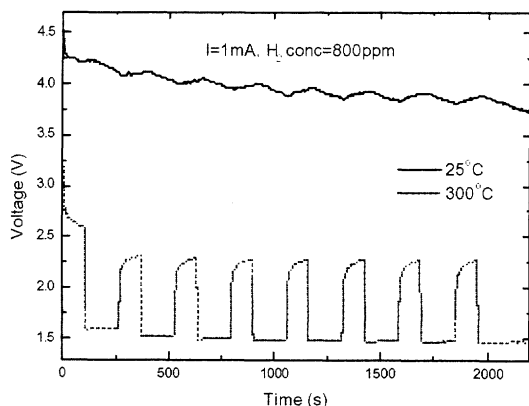


Fig.3 Response of NH₃-nitrided sensor upon alternate exposure to air and 800 ppm H₂ in N₂ at 25 °C and 300°C.

Fig.4 shows the sensitivity of the NH₃-nitrided sample and the control sample at different temperatures when the test chamber environment is changed from air to 800 ppm H₂ in N₂. The sensitivity is defined as $(I_{H_2} - I_{air}) / I_{air}$ where I_{H_2} and I_{air} are currents measured under hydrogen environment and air respectively. The applied voltage is 2 V. The sensitivity of the NH₃-nitrided sample is much higher than that of the control sample over the whole temperature range from 25 °C to 450 °C. The sensitivities of both samples first increase with temperature but then decrease as temperature further increases. This phenomenon can be explained as follows. When temperature increases, hydrogen molecules can decompose faster to hydrogen atoms on the surface of the electrode. Thus, more hydrogen atoms can diffuse through the electrode and hence increase the sensitivity. On the other hand, further increasing temperature can activate the traps inside the nitride as well as the traps at the metal/nitride interface, thus decreasing the sensitivity.

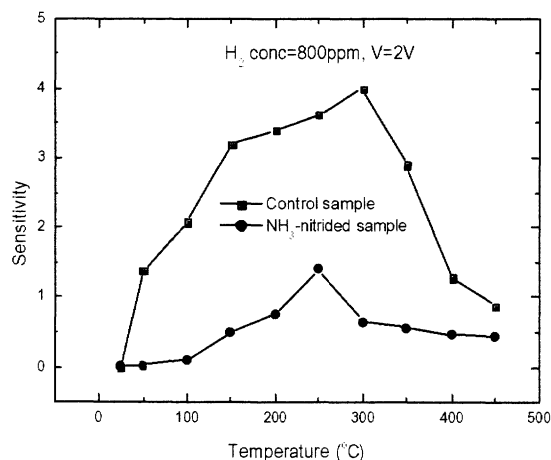


Fig.4 Sensitivity of the samples at different temperatures when the test chamber environment is changed from air to 800 ppm H₂ in N₂ under V= 2 V

Presented in Fig.5 is the sensitivity of the NH₃-nitrided sample upon exposure to different H₂ concentrations in N₂ at 300 °C. It is found that the sensitivity increases with decreasing applied voltage. It is because the smaller the forward bias, the smaller is the leakage current I_{air} and hence the higher is the sensitivity.

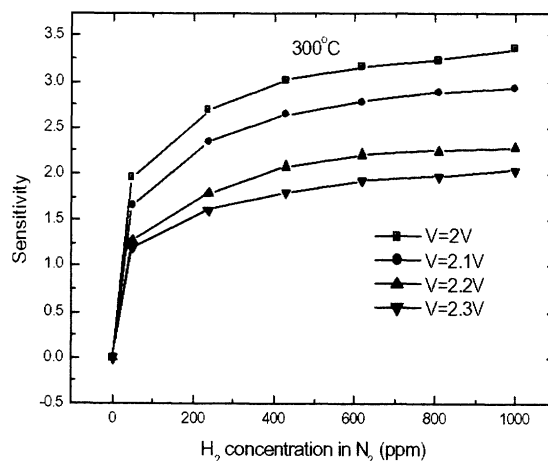


Fig.5 Sensitivity of the NH₃-nitrided sample upon exposure to different H₂ concentration in N₂ at 300 °C.

The sensitivity of the NH₃-nitrided sample upon exposure to different H₂ concentrations in N₂ is compared with that of the control sample in Fig.6. At 300 °C under a forward voltage of 2 V, sensitivities of both samples increase with hydrogen concentration. The control sample has a sensitivity of 6 % at 48 ppm H₂ and gets saturated very quickly at 429 ppm with a sensitivity of about 19 %. However, the NH₃-nitrided sample can give a significant response (sensitivity of 200 %) at 48 ppm H₂ and its sensitivity continuously increases to 350 % at 800 ppm and does not get saturated even at 1000 ppm. The enhanced sensitivity of the NH₃-nitrided sensor is due to the effect of NH₃ nitridation which improves the interfacial properties of the sensor. Excellent response of this sensor to hydrogen is further confirmed through continually changing hydrogen concentration, which gives rise to a rapid and clear "step" response as shown in Fig. 7.

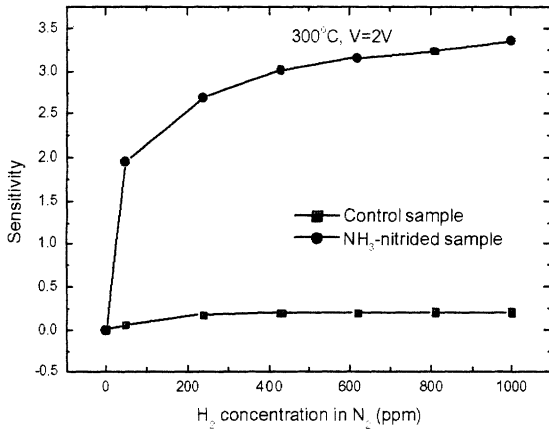


Fig.6 Sensitivity of the NH₃-nitrided and control samples (bias voltage = 2 V) upon exposure to different H₂ concentrations in N₂ at 300°C.

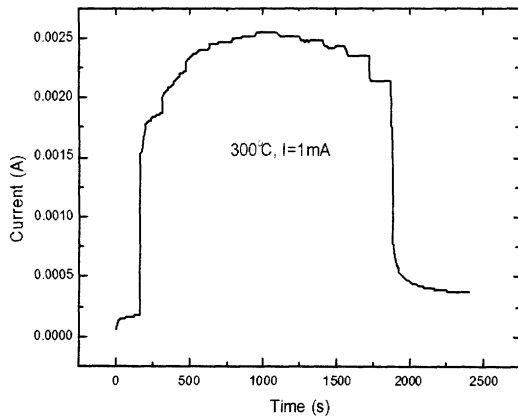


Fig.7 Response characteristics of the NH₃-nitrided sample when continually changing H₂

Fig.8 shows the change in the barrier height of the NH₃-nitrided and control sample upon exposure to different H₂ concentrations. Based on equation (2), the barrier height is calculated using the following formula:

$$\phi_b = -\phi_T \ln \left(\frac{I_o}{AA^{**}T^2} \right) \quad (3)$$

I_o (in air and in H₂) can be found from the corresponding y-intercepts of the graph (ln I vs V). When hydrogen concentration increases, the barrier height of the sensor decreases and the barrier-height variation defined as ϕ_b (air) - ϕ_b (H₂) increases. It is because when more hydrogen-containing molecules come to the front electrode, more hydrogen atoms can be absorbed at the electrode-nitride interface to form a polarized layer. This polarized layer causes a significant barrier lowering effect. The wider range of barrier-height variation in the NH₃-nitrided sample indicates that the sensor is more sensitive.

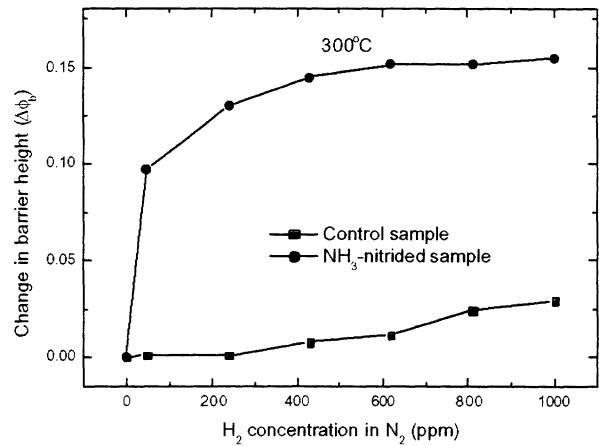


Fig.8 Barrier-height variation of the NH₃-nitrided and control sample upon exposure to different H₂ concentrations in N₂ at 300 °C.

According to the hydrogen reaction kinetics, the hydrogen coverage θ at the interface under steady-state condition can be written as

$$\frac{\theta}{1-\theta} = k_o \sqrt{P_{H_2}} \quad (4)$$

where k_o is a rate constant and P_{H_2} is the hydrogen partial pressure. The change in voltage across the hydrogen dipole layer, ΔV is proportional to the hydrogen coverage θ (i.e. $\Delta V \propto \theta$) and the proportionality constant is ΔV_{max} (maximum voltage change at a fixed temperature). By substituting the formula $\Delta V = \Delta V_{max} \theta$ into equation (4),

$$\frac{1}{\Delta V} - \frac{1}{\Delta V_{max}} = \frac{1}{k_o \Delta V_{max} \sqrt{P_{H_2}}} \quad (5)$$

By using equation (1), equation (5) can be written as

$$\frac{1}{\ln(I_{og}/I_o)} = \frac{1}{\ln(I_{ogmax}/I_o)} \left(1 + \frac{1}{k_o \sqrt{P_{H_2}}}\right) \quad (6)$$

where I_{og} and I_{ogmax} are the corresponding and maximum saturation currents in hydrogen environment respectively. As can be seen in Fig.9, the plot of $1/\ln(I_{og}/I_o)$ vs $(1/P_{H_2})^{1/2}$ gives a straight line, confirming the hydrogen reaction kinetics in the NH_3 -nitrided Schottky diode.

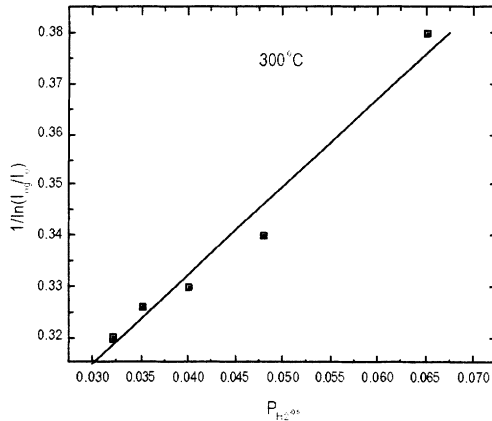


Fig.9 Steady-state reaction kinetic analysis for hydrogen absorption of the NH_3 -nitrided sample at 300 °C.

IV. SUMMARY

A novel NH_3 -nitrided Schottky-diode hydrogen sensor has been fabricated and studied. The influences of hydrogen concentration and temperature on hydrogen sensing performance of the device are investigated. Experimental results show that the sensor demonstrates high sensitivity, high stability, and fast response especially at a high operating

temperature of 300 °C. These properties provide the sensor potential applications for detecting hydrogen leakage in harsh environments. The study has shown that the barrier height of the device decreases upon hydrogen adsorption and this leads to an increase in its forward current. It is also found that the current-conduction mechanism of this sensor is controlled by the thermionic emission mechanism. The hydrogen reaction kinetics in the device is also confirmed.

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