A HYDROGEN SENSITIVE Pd/GaN SCHOTTKY DIODE SENSOR

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Abstract: *In this work, the forward current of Pd/GaN Schottky diodes is found to increase significantly upon introduction of H_2 into an N_2 ambient. Analysis of the current-voltage characteristics as a function of temperature shows that the current increase is due to a decrease in effective barrier height through a reduction in metal work function upon absorption of hydrogen. Experimental results also reveal that during the hydride formation process, the forward current is increased by the increase of temperature for hydrogen. This work also demonstrates that the Schottky barrier height indeed increases with increasing temperatures, and the resistance of the Pd/n-GaN device decreases with increasing temperature.*

Keywords: hydrogen sensor, Schottky barrier height, high temperature, Schottky diodes

1. INTRODUCTION

Micro chemical or biochemical sensors have become increasingly important subjects of research in the past several years as the need for chemical recognition elements and transducers grows. In addition, much attention has been paid to the hydrogen sensing technology in harsh environment, such as industrial manufacturing process, protection of environment contamination and biomedical detection at high pressure and high temperature. These conditions has spurs the development of wide band gap semiconductor gas sensors because of their potential for high temperature operation, chemical inertness and the ability to integrate them with power or microwave electrodes. Such high-temperature gas sensors can also be realized using wide-band-gap group-III nitride materials (GaN, AlN).

Recently, Pd-GaN Schottky diode has been shown to respond to hydrogen species. Palladium (Pd) is an attractive membrane material for hydrogen sensors due to their excellent catalyst performance and the promise of small integration with other device such as an amplifier to produce higher sensitivity. Initial work started using Pd in hydrogen detection devices based on the Pd-thin oxide Si (MOS) structures [1–3]. These devices exhibited the capability of detecting hydrogen concentration in the part per million ranges. Additionally, the Pd-ZnO Schottky diode showed a similar sensitivity with a tenfold increase in reverse saturation current on exposure to 1% H_2 in air [3–4]. In all of the reported devices, the decrease in Schottky barrier height was observed upon hydrogen adsorption. On the other hand, solid-state hydrogen sensor based on the III-V compound semiconductor devices is expected to have the merit of III-V material.

In this paper, we demonstrate the merits of a new hydrogen sensitive Pd membrane/semiconductor (Pd/GaN) Schottky diode sensor in terms of its thermal stability, chemical inertness and durability. This device shows good hydrogen sensitivity and can easily co-integrate with other GaN-based semiconductor devices such as photo detector or light emitting diode.

2. EXPERIMENT

In this study, Pd/GaN sensor was fabricated on n-type GaN ($1–3 \times 10^{17}$ cm^{-3}, 3–5 μm thickness) layer grown on Si substrates by the deposition of Pd by thermal evaporation coating (Edward 306) at pressure of 5×10^{-5} Torr. Clean surfaces were prepared by the following procedure. Prior to the metal deposition, the native oxide was removed in the NH_4OH:H_2O (1:20) solution, followed by HF:H_2O (1:50). Boiling aqua regia, HCl:HNO_3 (3:1) was used to chemically etch and clean the samples. A rectifying contact of Pd was deposited by thermal evaporator (Edward 306) at base pressure of at least 5×10^{-5} Torr onto the GaN metal mask.

After deposition, the samples were annealed under flowing Ar gas environment in the furnace at 600°C for 6 minutes, and the film was cleaned and dried for 1 h at 80°C. The gas sensing experiments were carried out in a homemade testing chamber using air, N_2 and 2% H_2 in N_2 gases at a total pressure of 1 atm and over a range of temperatures 273–773K. Before the measurement, the sample was pre-heated by heating it to 500°C and cooling it to 50°C. This step was repeated three times before starting film characterization in order to remove the water vapour. Measurements were performed at temperatures from 25–500°C in flowing gas ambient of pure N_2, a premixed 2% H_2 in N_2 and normal air. The current-voltage (I-V) characteristics of the studied device were measured for gases at different temperatures by a Keithley 237 source-measurement unit for current-voltage (I-V) measurements.

3. RESULTS AND DISCUSSIONS

The forward-biased I-V characteristics of the device at different temperature for hydrogen are shown in Figure 1. Clearly, the hydrogen-excited current as large as 70 mA is seen at forward-biased voltage of 0.5 V under hydrogen at 573K (373°C). This interesting phenomenon is mainly due to the hydrogen formation process. When hydrogen gas diffuses into the Pd coating surface, the hydrogen molecules will dissociate into hydrogen atoms. Some of the hydrogen atoms diffuse through the thin metal layer and form the Pd hydride near the metal-semiconductor interface. The hydride can effectively lower the work function of Pd metal. The lowering of work function results in the reduction of Schottky barrier height at Pd-GaN interface and modification in the measured I-V characteristics.

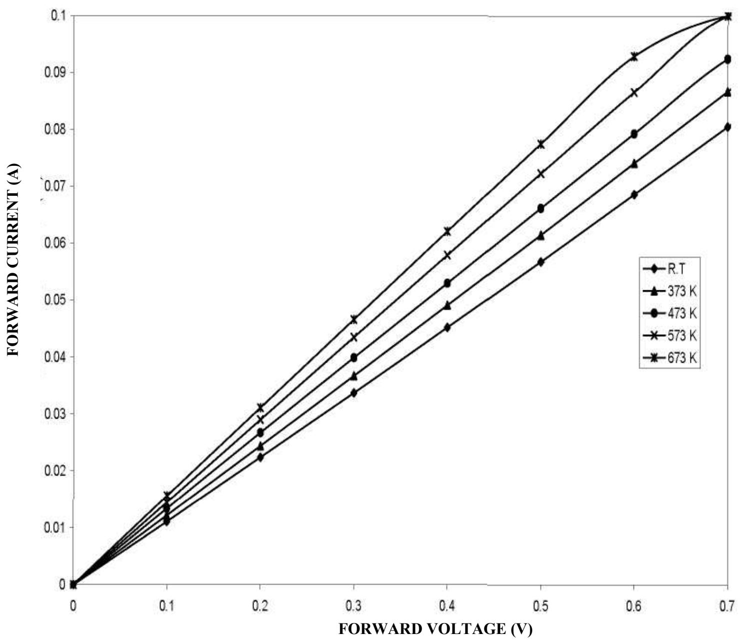

Figure 1: Forward I-V characteristics for hydrogen as a function of heating temperature

Figure 2 shows the reversed I-V characteristics of hydrogen as a function of heating temperature. The controlled different temperatures are supplied at 373K for hydrogen. Obviously, the current increases with the increase of temperatures, especially when the external reverse bias voltage is relatively larger. This also demonstrates that the increase of the hydrogen concentration is indeed helpful to lower the Schottky barrier height of the device.

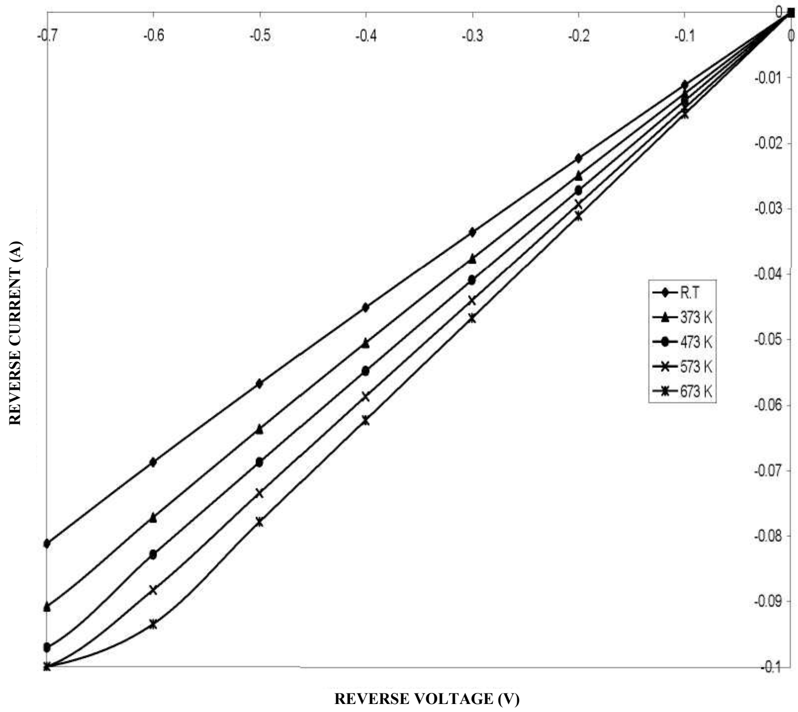

Figure 2: Reverse I-V characteristics for hydrogen as a function of heating temperature

The influence of the temperature dependent of hydrogen on the Schottky barrier height shift is shown in Figure 3. This is measured under a current saturation. Clearly, the barrier height shift increases with the increase of temperature. Furthermore, a nearly linear relationship between the barrier height and temperature is obtained. This significant property is suitable for practical application. This phenomenon can be understood as already described. The number of hydrogen atoms diffused from the Pd membrane surface to metal-semiconductor (Pd-GaN) region increases with increasing temperature. This certainly causes the magnitude of the Schottky barrier shift to increase.

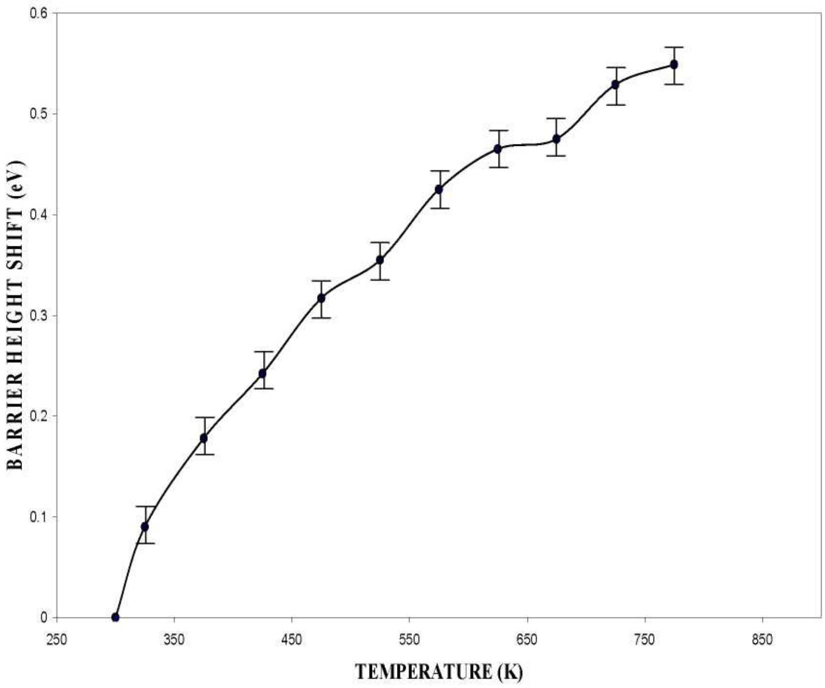

Figure 3: Temperature dependent of Schottky barrier height for hydrogen

A new hydrogen sensitive Pd/GaN Schottky diode has been fabricated successfully. It is known that, from the experimental results, the introduction of hydrogen gas exhibits a considerable sensitivity both under forward- and reverse-biased condition. Furthermore, a nearly linear relation between the Schottky barrier height shift and the temperature is obtained. This appears promising for practical sensor applications. Therefore, the sensing characteristics of the studied Pd/GaN Schottky diode can be combined with the other III-V device (e.g., high speed transistor, laser) to form excellent and functional intelligent integrated sensor circuit. To determine the potential for using GaN as a gas sensor, the resistance of GaN thin films was measured on a hotplate at elevated temperatures from 273 to 773K. The resistance of the Pd/n-GaN device decreased with increasing temperature as shown in Figure 4 which is a general property of semiconductors. In contrast, the Pd/n-GaN samples in the N_2 ambient exhibited a higher resistance than the H_2 within the temperature range used in this study. This is because the H_2 forms Schottky contact on the GaN surface, widening the space charge region, and hence increases the resistance to some degree.

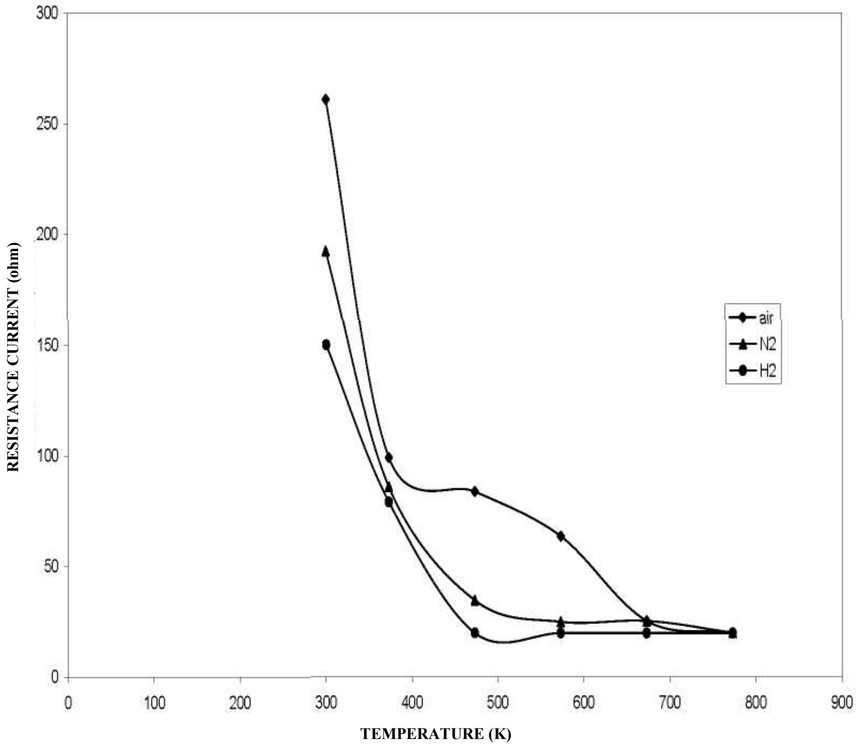

Figure 4: Resistance variation of Pd/GaN in air, N_2 and H_2 ambient

4. CONCLUSION

Pd/GaN Schottky diode was examined for their temperature dependence sensing characteristic upon introduction of hydrogen into the ambient. Significant decreases in barrier height were observed, leading to an increase in forward current. The Pd/GaN diodes show larger changes in current, due to more effective catalytic dissociation of H_2. The GaN materials system appears to be very promising for use in combustion gas detection, especially as part of integrated sensor structures that could also detect UV radiation.

5. ACKNOWLEDGEMENTS

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