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RESEARCH ARTICLE

Applications of hydrogen sensing of concentrations for Pd/SiO_2/GaN Schottky diode

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ABSTRACT

In this work, the Pd/SiO_2/GaN Schottky diode have been fabricated and characterized for H_2 sensing. Using both forward- and reverse current–voltage (I–V) characteristics we have found that the Pd/SiO_2/GaN Schottky diode sensor exhibited very high sensitivity towards hydrogen concentrations at various temperatures. From experimental results, the studied device demonstrated excellent sensing performances and fast response and recovery rates compare to Pd/GaN. The decrease in the barrier height of the diode was calculated to be about 160meV upon introduction of 10% H_2 into the ambient. The sensitivity of the sensor is also calculated. Some thermodynamics analyses have been done according to the Langmuir isotherm equation. Scanning electron microscopy (SEM) was used to examine the porosity of the GaN surfaces. SEM pictures showed highly porous structures of the contacts provided for penetration of hydrogen gas molecules.

Keywords: GaN; Schottky diode; Hydrogen concentrations; barrier height.

INTRODUCTION

Hydrogen is a technologically important gas used in many industries, such as semiconductor processes, metallurgy, chemical processing, and in refining (DiMeo *et al.*, 2006). Recently, hydrogen has gained a lot of attention as a novel source of energy due to its efficiency and high energy output and because it does not pollute air. However, hydrogen is a flammable and explosive gas. When the hydrogen concentration in air is greater than 4%, a hazardous explosion will occur. Thus, it is necessary to develop a safety monitoring system for detecting the hydrogen level using an accurate sensor. The hydrogen sensor should work in a low hydrogen concentration, can be operated at room temperature, and wide hydrogen concentration range environment. In addition, a short response time is also a critical requirement for hydrogen detection in real time applications. Based on the chemical, optical, and electronic transduction methods, difference-type hydrogen sensors were designed and reported in the past (Ibanez and Zamborini, 2006; Zhao et al., 2006; Chou *et al.*, 2005). Electronic-based hydrogen sensors involving catalytic metal, such as pyroelectronic (Christofides and Mandelis, 1990), electrochemical (Lutz *et al.*, 2005), chemiresistive (Xu *et al.*, 2005), and semiconductor/field effect sensors (Tsai et al., 2006a; Cheng *et al.*, 2005), have recently played an important role in hydrogen sensing technology. A number of studies on diode-type hydrogen sensors based on the change of Schottky barrier height at the catalytic metal electrode for a sensing function of hydrogen concentration have been investigated (Tsai *et al.*, 2006; Chen *et al.*, 2002). In comparison with capacitive devices, the advantage of the Schottky diode is its simplicity in electronic circuitry required for the operating sensors. Moreover, the hydrogen sensors made by metal-oxide-semiconductor (MOS) type of Schottky diode using compound semiconductor materials of wider band gap such as SiC and GaN have been developed and applied in a high temperature environment (Kandasamy *et al.*, 2005; Song *et al.*, 2005). It is because a large band gap may result in high electron saturation velocity and high breakdown field strength. Furthermore, the MOS structure has better thermal stability than the metal-semiconductor structure and is well-suited to hydrogen sensing (Khan *et al.*, 2000). The promising potential of MOS structure in hydrogen sensing was first pointed out by undström (Lundström, 1981, 1982). In this paper, Pd/SiO_2/GaN MOS-type Schottky diodes have been fabricated and measured for H_2 sensing. The sensor's responses under different H_2 concentrations from 500 ppm H_2 to 10% H_2 in N_2 are investigated. The time responses in N_2 and air atmosphere at 300K and 515K are measured. The variation of the Schottky barrier height of the sensor is calculated according to the thermionic emission theory.

MATERIALS AND METHODS

The studied Pd/SiO_2/GaN MOS-type Schottky diode-based hydrogen sensor was grown by a metal organic chemical vapor deposition (MOCVD) system on 2-inch *c*-plane sapphire substrates. The epitaxial structure consisted of a 2μm thick undoped GaN buffer layer and a 0.5μm Si-doped GaN active layer with a carrier concentration of $2\times10^{18}cm^{-3}$. After epitaxial growth, the devices were etched by an inductively couple plasma reactive ion etching system for mesa isolation. The native oxide on the wafer was removed by a solution of HCl: H_2O=1:1. The Ohmic contact, formed by evaporation 100 nm thick Ti/Al metals, was subsequently annealed by rapid thermal treatment at 900°C for 90s in an N_2 ambience. Then, the sample was immediately put into the oven under dry oxygen environment to form a fresh thermal oxide layer to produce the desired MOS structure. Most of the experiments were performed at 300K and 373K, with flowing gas of N_2, H_2 diluted in N_2 and air. Finally, the Schottky contact was produced by the evaporation of Pd metal on the surface of the thin oxide layer. The Pd metal thickness and effective area were 150 Å and $2.05\times10^{-3}cm^2$, respectively. The hydrogen sensing set-up of apparatus is includes four parts, i.e. gas cylinders, a temperature control system, a hydrogen testing chamber and electric read-out system. The gas cylinders supply the background gas and testing gases.

RESULTS AND DISCUSSIONS

The current–voltage (I–V) characteristics of the Pd/SiO_2/GaN Schottky diodes exposed to pure N_2 and 10% H_2 in N_2 at 300K are shown in Figure 1. Both the forward and reverse currents of these sensors increase greatly when exposed to the hydrogen gas. The sensors can be operated under forward and reverse applied biases and exhibit remarkable hydrogen detecting capability.

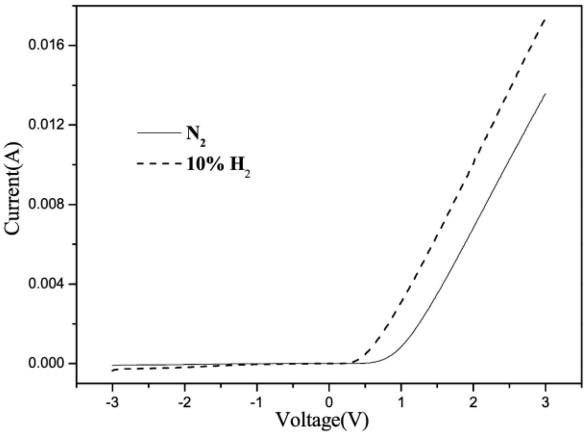

Fig 1: I–V characteristics from the diode measured in N_2 or 10% H_2 in N_2 ambient at 300K.

Figure 2(a) shows the time response of forward current of the diode biased at 0.5V in different atmosphere (N_2 10% H_2 in N_2 and air) at 300K. Even at room temperature, the change in forward current for a fixed bias of 0.5V is detectable and shows there is sufficient cracking of the H_2 for the diode to be a sensitive gas detector. It could be seen that the rising curve is very steep and the turn-on response of the sensor is relatively quick; the turn-off response in N_2 is relatively slow, while the turn-off response in synthetic air is relatively quicker.

When the flow of H_2 is shut off at 7 min, the electrical signal (current) is observed to increase, this is illogical. Authors are requested to give an explanation for this unusual phenomenon. For H_2 detection, once the H_2 is turned on, the device normally will be able to sense the presence of H_2 instantaneously and current will increase sharply. This observation is contradicted to the H_2 sensing current transient reported in the literature. Because clearly, the current is increased proportionally with an increase of hydrogen concentration. All of the curves response rapidly from transient state to steady state upon hydrogen adsorption (H_2 on) and hydrogen desorption (H_2 off). This is due to the lowering effect of observed Schottky barrier height. When the sensing response is completed, the testing H_2 in air gas is cut-off, and the synthetic air gas is introduced into sensing system for recovery. The *I-t* curves for transient recovery are also recorded till the current is recovered to the baseline value. From Figure 2, we are note that there is different between the hydrogen concentration. In Figure 2(a) is 10% H_2 in N_2, while in Figure 2(b) is 1% H_2 in N_2.

Figure 2(b) shows the time response at 373K of the forward current of the diode biased at 0.5V. It can be seen that though the concentration of the hydrogen is decreased, the response of the sensor at 373K is still high; the turn on and turn off response have similar curves, the recovery time is greatly decreased when the sensor is exposed to the synthetic air at 373K. The higher temperature could accelerate hydrogen molecule to decompose, adsorb, diffuse and desorbs, so the response time and recovery time are getting shorter. It seems that the oxygen in the air could react with the hydrogen atom to produce water and inhibit the hydrogen to adsorb at the metal's surface and the number of the hydrogen covered at the interface of the metal and the semiconductor is reduced (Huang *et al.*, 2007).

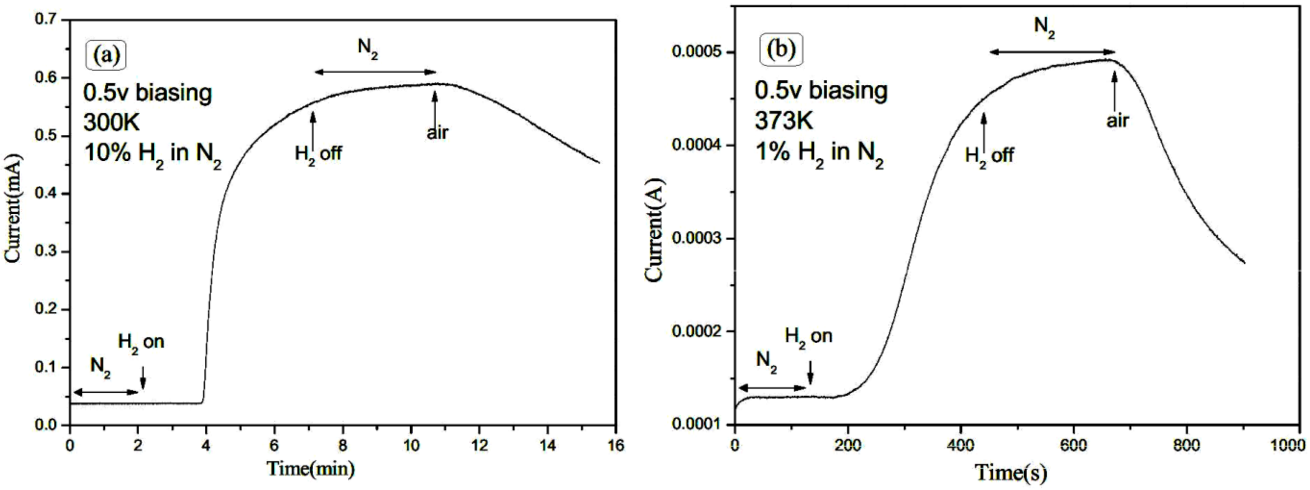

Figure 2: Time response (a) at 300K and (b) at 373K of the forward current of the diode biased at 0.5V, the gas flows in the sequence of N_2, H_2 in N_2 and air.

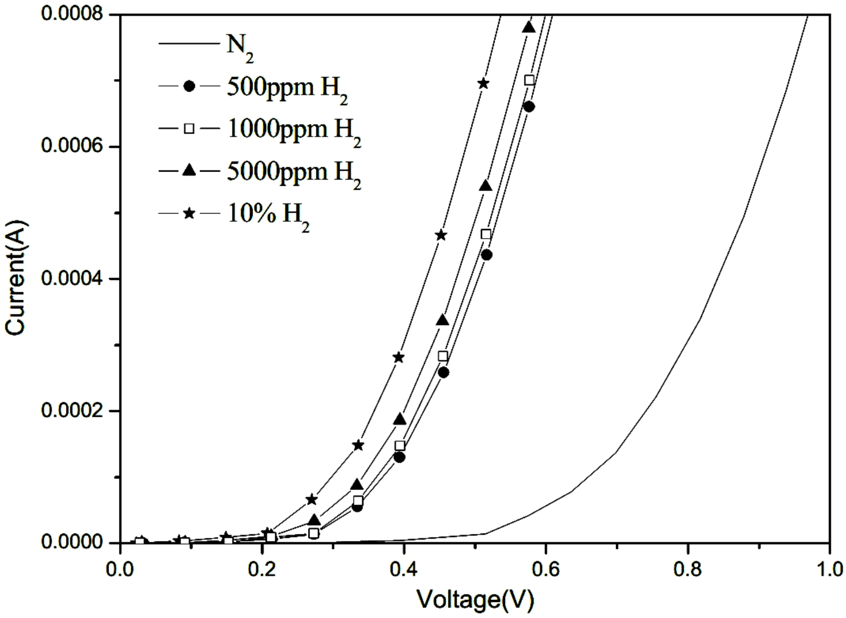

Figure 3: Forward-bias I –V characteristics of Pd/SiO$_2$/GaN Schottky diode at 300K in pure N_2 and in N_2 containing H_2 between 500 ppm and 10%.

The *I–V* curves in Figure 3 are measured at 297K in N_2 and in H_2/N_2 mixtures with the H_2 concentrations increasing from 500 ppm to 10%. The forward bias characteristics show that the diode voltage, at a current of 0.5mA, shifts from 0.88V in N_2 to 0.53V in 500 ppm H_2 and to 0.46V in 10% H_2. It can be seen that 500 ppm hydrogen has already made the *I-V* curve shift greatly; as the H_2 concentration increases further, the *I-V* curves shift further to the lower voltages. When increasing the operating temperature, hydrogen concentrations less than 500 ppm can be detected. It seems that at 300K the cracking efficiency maybe not high enough to decompose the hydrogen molecules when the hydrogen concentration is low.

The sensitivity of the sensor can be defined by the following equation:

$$S = \left(I_{H_2} - I_{N_2}\right) / I_{N_2}$$

where I_{H_2} and I_{N_2} are the current levels in H_2 containing ambient and in N_2 ambient, respectively. From Figure 4, a sensitivity of 47.7 at 0.5V biasing can be obtained when the sensor is exposed to 10% hydrogen. According to the thermionic emission theory (Schroder, 1990), the current of the Schottky diode can be described as:

$$I = I_s \left[\exp\left(\frac{q(V - IR)}{nkT} \right) - 1 \right],$$

$$I_S = AA^{**} T^2 \exp\left(\frac{-q\phi_b}{kT}\right)$$

where *A* is the area of the Schottky contact, *A*** is the Richardson constant for n-GaN (24 $Acm^{-2}K^{-2}$), *T* is the temperature in Kelvin, Φ_b is the Schottky barrier height, *V* is the bias voltage, R is the series resistance, *k* is the Boltzmann constant and *n* is the ideality factor equal to 1 (*n* = 1) in the case of sole thermionic emission (Zdansky and Yatskiv, 2012). The other parameters have commonly known meanings and their values are known (Zdansky *et al.*, 2007; Sze, 1969). The decrease in effective barrier height is obtained from fitting the forward *I–V* characteristics over the low bias range (<1*V*) to the relation for thermionic emission over a barrier.

Figure 4 gives Schottky barrier height as a function of the hydrogen concentrations. As the hydrogen concentration increases, the Schottky barrier height decreases. From 500 ppm to 5000 ppm H_2, the barrier height decrease greatly. When the hydrogen concentration increase above 5000 ppm, the barrier height decreases slowly.

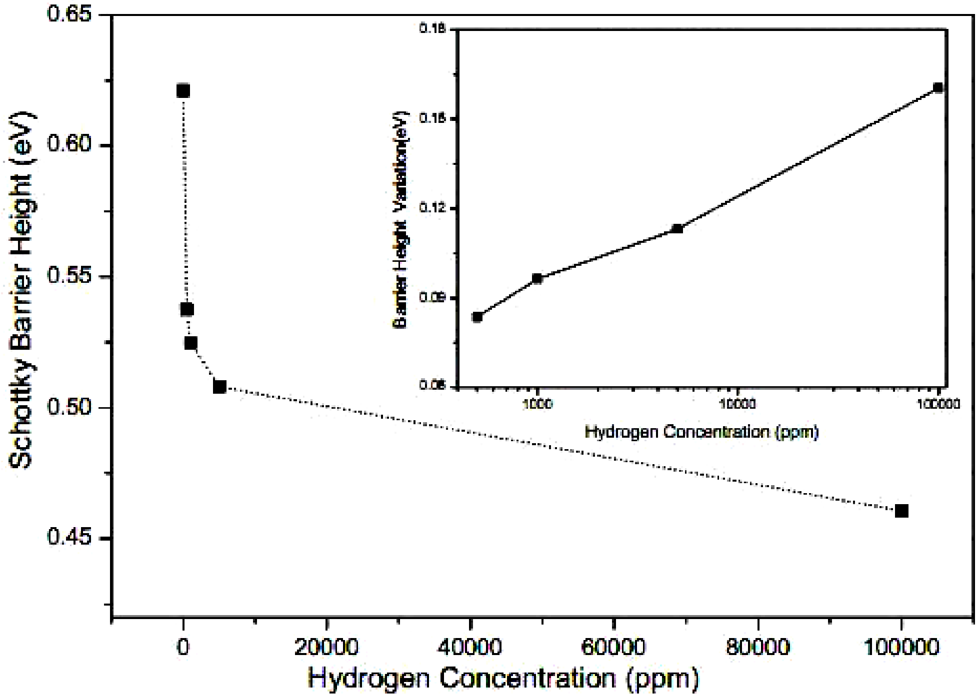

Figure 4: Schottky barrier height as a function of the hydrogen concentrations

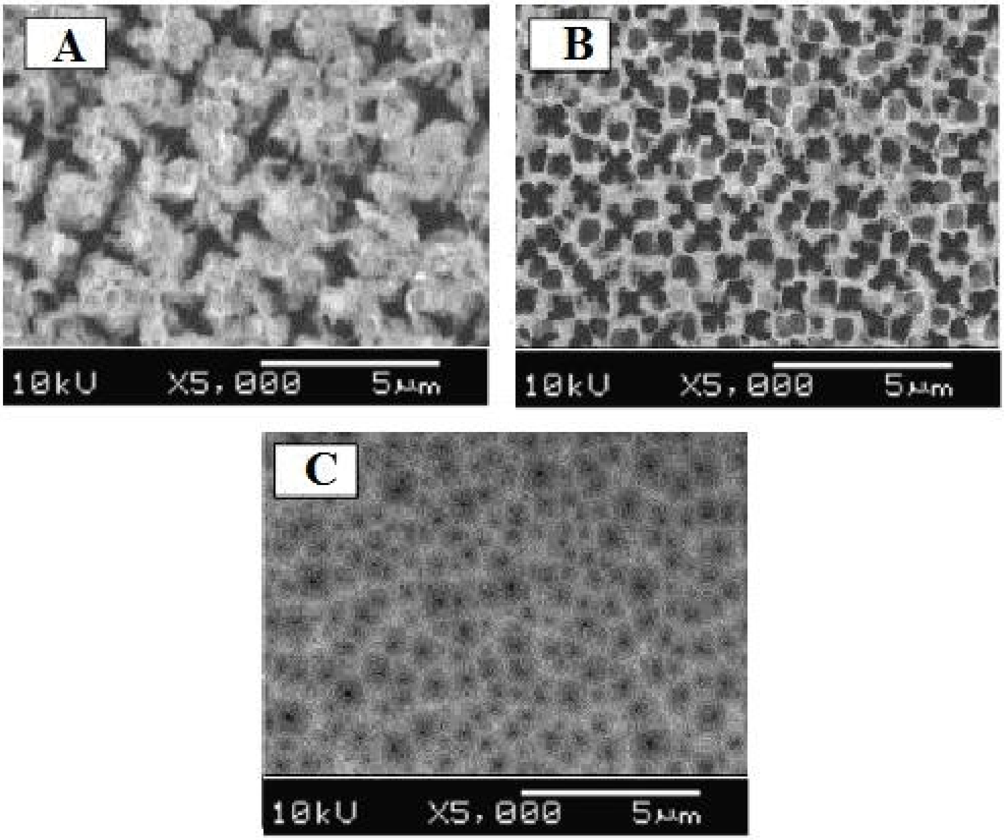

Figure 5: SEM images of Pd/SiO_2/GaN Schottky diodes at 300K in N_2 containing H_2 at: (A) 500 ppm, (B) 5000 ppm and (C) 10%).

The change in the barrier height is about 160 mV at 300K upon introduction of 10% H_2 into the ambient for the sensor. The inset of Figure 4 gives the barrier height variation versus the hydrogen concentration. The figure demonstrates a good linear relationship between the barrier height variation and the hydrogen concentrations (in log axis).

SEM images observations were conducted for samples exposure at 300K in N_2 containing H_2 at (500 ppm, 5000 ppm and 10%) in order to examine the porosity of the Pd/SiO_2/GaN Schottky diode and to show the surfaces changes of the surface morphology. As show in Figure 5 metal surface showed a surface for exposure hydrogen at room temperature. When the concentration of hydrogen increase islands appeared on the surface. Island formation upon exposure hydrogen of Pd/SiO_2/GaN Schottky diode is explained with the difference of surface energies thin metal films and Pd/SiO_2/GaN Schottky diode that causes rewetting. The formation of the island may lead to the decrease of the mean surface density. SEM pictures showed highly porous structures of the contacts provided for penetration of hydrogen gas molecules.

CONCLUSION

In conclusion, we have fabricated and characterized Pd/SiO_2/GaN Schottky diodes for H_2 sensing. Both the forward and reverse current of the device increase when exposed to H_2 gas. A shift of 0.45V at 300K is obtained at a fixed forward current for switching from N_2 to 10% H_2 in N_2 and the corresponding decrease in the barrier height is calculated to be about 160meV. No saturation phenomenon occurs when H_2 concentrations increase from 500pm to 10% at 300K. Time response of the sensor at a fixed bias of 0.5V is also measured. The turn-on response of the device is rapid (within tens of seconds), while the recovery of the sensor at 300K is rather slow. The recovery time is greatly decreased when the sensor is exposed to the synthetic air at 373K. Good linear relationship between the barrier height variation and the hydrogen concentrations has been found. A sensitivity of 47.7 at 0.5V biasing can be obtained when the sensor is exposed to 10% hydrogen. SEM pictures showed highly porous structures of the contacts provided for penetration of hydrogen gas molecules.

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