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Effect of porosity on GaN for hydrogen gas sensing

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ABSTRACT

Porous wide bandgap semiconductors have been widely studied in the last decade due to their unique properties compared to the bulk crystals. The high surface area, shift of bandgap, luminescence intensity enhancement and efficient photoresponse when porosity is formed can be tailored to fabricate new sensing devices. In this work, porous GaN was prepared by ultraviolet (UV) assisted electroless chemical etching method. The commercial Si doped n-type GaN film grown on two inches diameter sapphire (0001) substrate with GaN thickness of 5.5 µm was used in this study. The wafer was then cleaved into few pieces, and these samples were etched in $HF:H_2O_2:CH_3OH$ under UV illumination for 60 minutes. The structural properties was characterized using Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM). Hydrogen sensor was subsequently fabricated by depositing Pt Schottky contact onto the porous GaN sample. The effect of sensing dilute H_2 gas with different concentration which is 1% and 2% H_2 in a N_2 gas ambient was analyzed. The Schottky barrier height of the gas sensor samples was reduced upon exposure to gas. The porous GaN resulted better sensitivity compared to the as grown GaN sample in H_2 gas sensing

| Porous GaN | Pd Schottky contact | Gas Sensing | Electroless Chemical Etching |

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1. INTRODUCTION

The fabrication of porous semiconductors has stimulated much research interest recently. Porous semiconductors show various important optical features compare to normal crystalline semiconductors such as higher intensity of photoluminescence emission, better photoresponce and shift of band gap [1].The research in porous GaN (PGaN) is strongly driven by the superior physical properties such as the excellent thermal, mechanical and chemical stability, as well as the potential shift of the bandgap [2]. The large bandgap on GaN ensures minimal problems due to unwanted optical or thermal generation of charge carriers (e.g high temperature gas sensors, etc) [3]. The wide bandgap materials possess low dielectric constants with high thermal conductivity pathways. They also exhibit strong lattice polarization effects which have been recognized as suitable for application to high temperature piezoelectronics and pyroelectric sensors [4]. The piezoelectric properties of GaN can be use to fabricate high frequency surface acoustic wave devices. Since porous GaN has a higher surface/volume ratio than crystalline GaN, it could also function as a gas or solution sensor based on changes in photoconductivity during exposure to analytes [5, 6].

The determination of hazardous hydrogen concentration in air is an important issue in many areas of human activity (e.g medical installations, laboratories and fuelled motor vehicles) [7]. The combination of Pd-Schottky contacts with GaN is very sensitive to hydrogen exposure and is chemically resistant towards exposure of aggressive gases in air [6]. Molecular hydrogen, in the air or by itself, is absorbed at the metallic surface, where it undergoes a catalytic dissociation into atomic hydrogen.

The atomic hydrogen then diffuses very quickly towards the Pd-GaN interface and forms a dipole layer. The dipoles then cause polarization in direct proportion to the hydrogen ion concentration [8].

The dipole layer will be balanced by a modulation of the depletion layer, which leads to the change in the effective work function of the metal, thus changing the schottky barrier height and eventually change the electrical characteristics of the device [9,10].

This is a report to present gas sensing properties of Pd Schottky contact onto as grown GaN and porous GaN sample. By having a larger area per unit volume of the semiconductor, we can establish a comparable or better gas sensing device to those produced by the as grown materials. The effect of the gas sensing is proven by measuring current voltage (I-V) curves to calculate the Schottky barrier height for both samples after the gas exposure.

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2. EXPERIMENTAL

2.1 Materials

The samples used in this study were commercial n-GaN (Si doped) grown on sapphire (Al_2O_3) substrates. The electron concentration was (1~3) x 10^{18} cm^{-3}. The samples were cleaved into the dimension of 0.8 cm x 0.8 cm approximately. Prior to the metallization, the native oxide of the sample was removed in the 1:20 $NH_4OH:H_2O$ solution for 15 sec, followed by 1:50 $HF:H_2O$. Subsequently boiling aqua regia (3:1 HCl: HNO_3) was used to etch and clean the sample for 5 minutes. Between the cleaning steps, the samples were washed with distilled water and dried using nitrogen air gun to avoid forming of oxide layer.

2.2 Etching Process

Sample with Pt contact sputtered is placed into a solution with ratio of $CH_3OH:HF:H_2O_2$ 1:4:1 under 500 W UV illumination for electroless chemical etching method and leave for 60 minutes. The catalytic reduction of H_2O_2 at the Pt islands combines with UV illumination to inject holes deep into the valence band, which subsequently produces an etched porous structure. UV illumination is one of the photo-assist electrochemical etching technique and it is also categorized under wet etching techniques. UV illumination method was chosen due to its low processing cost and simple experimental procedure and versatility of its processes [11]. UV light illumination will provide more holes for oxidation thus affecting the etching rate.

2.3 Schottky Contact

After the etching, the sample was washed with distilled water using ultrasonic wave before being soaked in methanol to remove residual Pt. The etched samples (porous GaN) are pasted onto a holed mask to produce contact. For Schottky contact, palladium was sputtered and aluminium was evaporated on the surface. The surface morphology of the porous GaN samples were investigated by scanning electron microscope (SEM) (JSM-6460/LV JEOL) and atomic force microscope (AFM). Current-voltage (I-V) measurements were performed to monitor the change in the gas sensor samples with and without gas exposure.

3. RESULTS & DISCUSSION

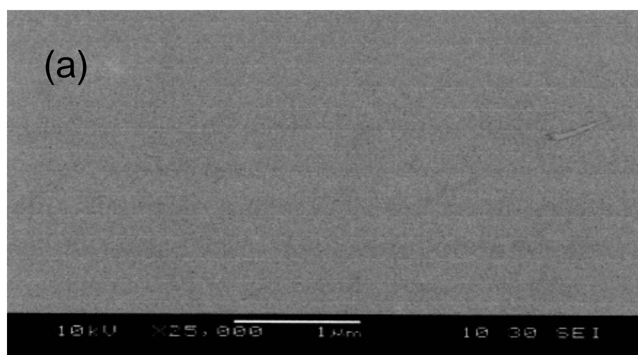
3.1 Surface morphology

SEM of morphology of the as grown and porous GaN samples was shown in Figure 1. The electroless chemical etching was done using ratio of 1:4:1 for the solution $CH_3OH:HF:H_2O_2$. From the SEM micrographs, the surface of the as grown GaN sample is smooth. There is no pores or any significant surface defects detects. For porous GaN sample in Figure 1(b) the surface of the sample viewed at 25k magnification was uneven. This is due to the etching process by illumination of UV lights towards the sample. A further investigation on the surface using 10k magnification as shown in Figure 1(c) infers that the surface of GaN sample after etching was consist of repeating structure. Furthermore, it can be observed that on the porous GaN, there were made up of ridges and trenches. Studies found that the etching proceeds by first forming a network in trenches between the ridges. As the etching progresses further, the sidewalls of the ridges become steeper, and then the ridges start to disappear. In all cases, the electroless deposition of metals on porous GaN (PGaN) was extremely sensitive to the conditions of the surface and plating bath [12].

It is interesting to note that from the tilted image revealed that there was a steep ridge sidewall with the porous network forming between the ridges in the trenches. SEM images revealed that the depth of the trenches were around 2~3μm. The GaN sample was grown with thickness of 5.5μm on sapphire substrate therefore, we can be sure that there is still ~2μm thick GaN in the trenches structure, and the sample was not over- etched. Therefore, precleaning to remove any pre-existing surface contaminant adlayer was imperative to obtain reproducible etching. An adlayer would adversely affect hole injection across the Pt GaN interface and lead to irreproducible etching due to the increased Schottky barrier height for Pt GaN [12].

Apart from that, investigation on the morphology of metal contact on the surface of porous GaN samples yielded the same surface morphology as the porous GaN surface without contact. For metal contacts to GaN, the condition of the surface was key in determining the electrical properties. The surface roughening due to a ‘balling up’ effect can induce the lack of lateral homogeneity and the degradation of contacts, which also had been widely observed in metallization process [13].

The palladium contact sputtered onto the surface of porous GaN take the physical structure of the GaN surface. The same case follows for aluminium contact evaporated onto the porous GaN surface too. While for as grown GaN sample, the surface for both the palladium contact and aluminium contact were smooth. The palladium and aluminium contact on porous GaN surface morphology will have an important role in the gas detection mechanism.



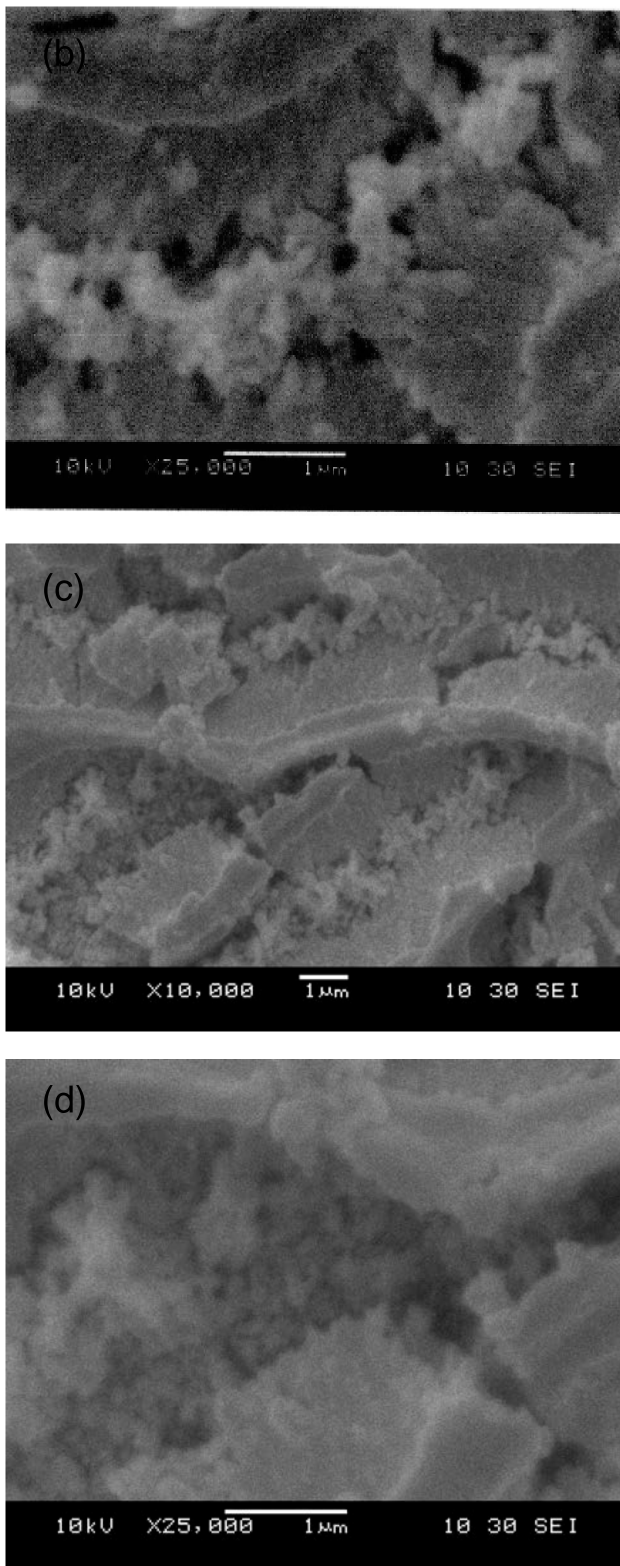


Fig. 1 SEM images of (a) as grown sample at 25K (b) porous GaN at 25K (c) porous GaN at 10K (d) porous GaN sample tilted at 30° at 25K magnification.

AFM analysis was performed to understand how the affects of morphology for as grown GaN and Porous GaN. Figure 2.0 (a) and Figure 2.0 (b) shows two dimensional AFM images of as grown GaN and porous GaN samples. Comparing two sample morphology it is shown that there is a noticeable change in surface morphology. The as grown sample is smooth than the porous GaN sample. The smooth surface shown the single crystallite layer of GaN deposited on sapphire substrate.

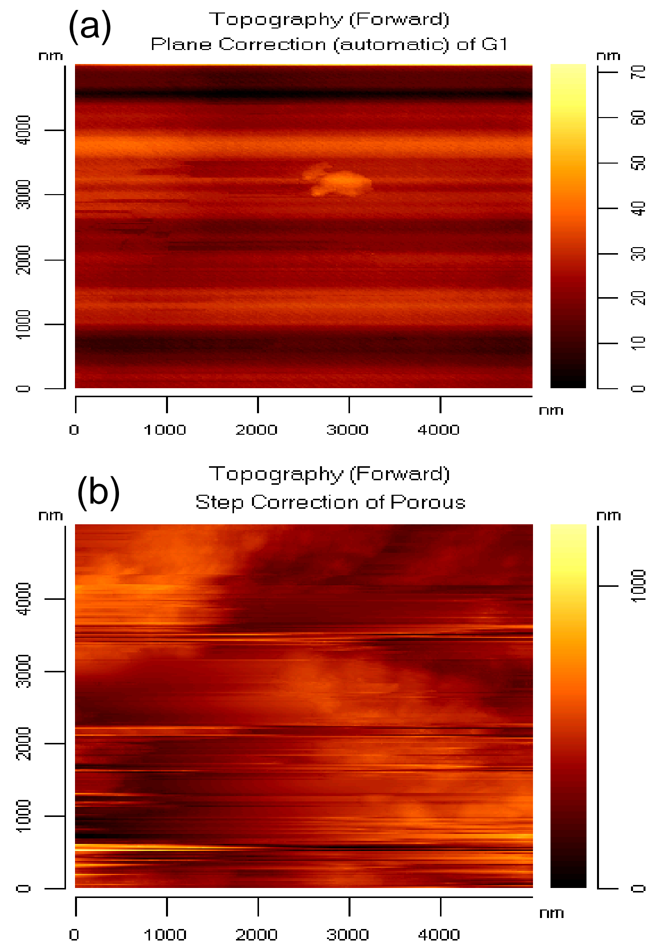


Fig. 2 AFM images of (a) as grown sample (b) porous GaN in 2D

Figure 3.0 (a) and 3.0 (b) showed three-dimensional AFM images. AFM morphology revealed a change in the roughness for porous GaN sample. The highest point roughness for the as grown sample was 71.49 nm while the highest point for the porous sample was 1200.21 nm. The surface roughness (RMS) for porous GaN sample was higher than as grown GaN sample. Surface roughness for porous GaN sample was 128.92 nm while as grown GaN sample was 7.36 nm. The roughness of the porous morphology could provide reaction sites for gas sorption [14].

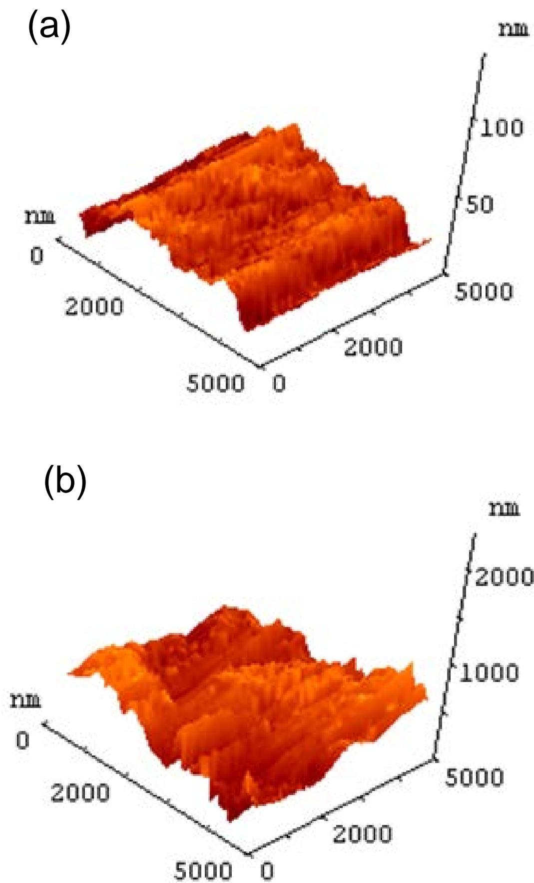


Fig. 3 AFM micrograph of the (a) as grown sample (b) porous GaN in 3D

3.2 I-V Characteristics

The current – voltage (I-V) characteristic data was used to further calculate the Schottky barrier height value for both as grown and porous sample before and after exposing to hydrogen gas. The sample used for I-V characteristics was placed in a stainless steel test chamber. The probe was placed on the aluminium contact while the other was probed onto the palladium contact. The I-V measurements were first taken manually from the power supply without the gas flow. After taking the measurements, the gas was then set to flow for 1 minute.

The hydrogen gas used in the experiments was mixture of the hydrogen gas and nitrogen gas, where the composition was 1% H_2 and 99% N_2 gas and the other composition was 2% H_2 and 98% N_2 gas. The diameter of the Schottky contact was 0.9 mm. Comparison will be made on the values of Schottky barrier height to determine the effect of hydrogen gas on the values.

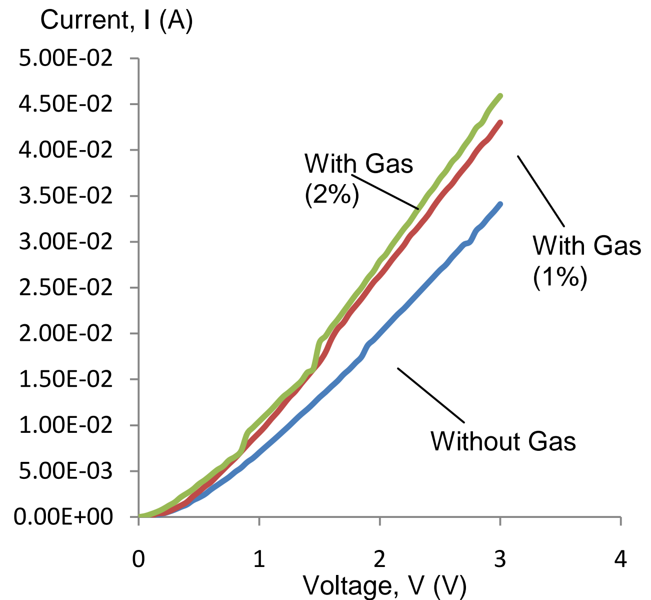


Fig. 4 Comparison of as grown sample without gas and with 1% and 2% H_2 gas response I - V curve.

The I-V curve for as grown sample response towards different gas concentration were shown in Figure 4. Analysis of I-V characteristics for as grown Pd/GaN Schottky diode showed that the forward current increased in H_2 containing ambient due to Schottky barrier height reduction caused by the formation of H induced dipole layer at the oxide interfacial layer. This strongly revealed that there were not too much difference with addition of 1% H_2 and 2% H_2 onto the samples. However from the calculation made, it was found that the introduction of 1% hydrogen gas into the ambient reduced the Schottky barrier height value, thus resulting in the corresponding increase in current as shown in the Figure 4.0 above. The reduction only 10 meV in Schottky barrier was observed for as grown GaN sample upon switching ambient to 1% hydrogen. While for the 2% hydrogen the value was almost similar as 1% hydrogen.

The lowering of the barrier heights due to accumulation of hydrogen at the Pt/GaN interface was consistent with the formation of the dipole layers at the interface [15]. Hydrogen accumulation at the interface changed the work function of the metal gate and therefore the barrier height of the Schottky contact was lowered. The gas adsorption at the surface of GaN Schottky diodes also leaded to measurable changes in the diode currents [16].

This effect can be proven by measuring current-voltage curves. The observed disparities in the measured barrier heights between the different authors maybe attributed to variations in material characteristics, measurement techniques used and sensitivity of the I-V and contamination on the probe used.

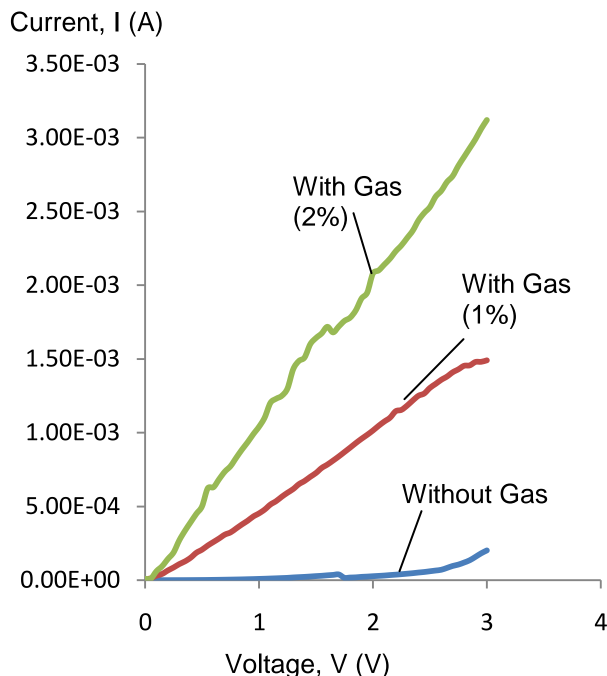


Fig. 5 Comparison of porous GaN sample without gas and with 1% and 2% H_2 gas response curve.

As for porous GaN sample, upon exposure to hydrogen gas ambient, the saturation current of Schottky barrier height increased drastically as shown in Figure 5.0. The Schottky characteristics deteriorated and Ohmic behaviour was observed. The dipole layer at the Pd-GaN interface was affected by hydrogen gas due to their reactivity, and the electric field under the Pd gate was altered thus producing the resulting change in diode forward current. The dissociation can occur through a catalytic reaction with the Pd gate through additional surface reactions on the semiconductor. This positive hydrogen concentration increased can be attributed to the increased collision among hydrogen atoms that induced a higher reaction rate.

The forward current of all the diodes increased with exposure to hydrogen gas, which attributed to the Schottky barrier reduction caused by atomic hydrogen absorption on the metal-oxide interface.

On the other hand, it is interesting to note that the porous GaN sample exhibited a more drastic difference than the as grown GaN sample upon exposure to the 1% and 2% hydrogen gas ambient. This clearly revealed that the porous GaN sample had higher sensitivity than the as grown GaN sample. GaN was chemically resistant towards exposure by all known aggressive gases in air and in combination with Pd-Schottky contacts very sensitive to hydrogen exposure . The Schottky barrier height from calculation done for porous GaN sample was 0.7eV. This result was similar to L. Wang et al [17].

Since the porous sample response at a certain value of voltage applied was relatively small as compared to the as grown sample response, thus, only straight lines for porous samples (with and without gas response) can be observed. These were shown in Figure 6.0.

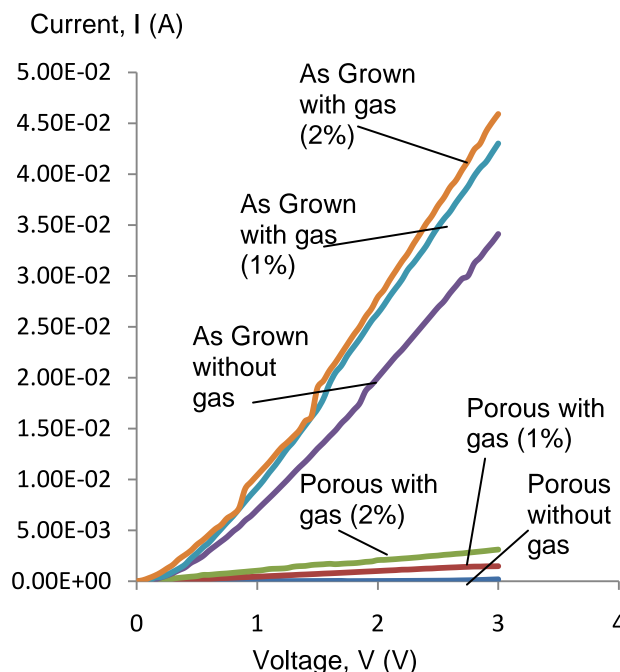


Fig. 6 Comparison of as grown GaN sample and porous GaN without gas and with 1% and 2% H_2 gas response curve.

From Figure 4.0 and 5.0, we can see that by increasing H_2 concentration, it showed an increase of the current, which can be attributed to a decrease in the Schottky barrier height. With increasing hydrogen concentration, the sample of porous shows a rapid increased in $\Delta ø_B$ compare to as grown GaN sample. This positive hydrogen concentration dependence can be attributed to the increased collision among hydrogen atoms that induced higher reaction rate and more hydrogen atom trapped at the semiconductor interface. In a constant current operation mode, this reduction of the Schottky barrier height resulted in a shift to lower bias voltage, which constituted the sensor signal.

According to Ali *et al* [18], the sensitivity to H_2 was investigated in dependence on the active area, metal contact thickness and the operating temperature. A significant increase of sensitivity has been observed by increasing the temperature of operation and decrease the metal contact thickness. However, the effect of the different thickness of the catalytic metals to the hydrogen sensing sensitivity of the devices pose as a problem yet to be solved in the future research activities.

On the other hand, the higher sensitivity in the porous GaN sample as compared to the as grown GaN sample was attributed to the larger area per volume ratio of the GaN sample. This due to the more surface of the GaN was exposed to the hydrogen gas, the more dipoles were formed at the Pd-GaN interface while maintaining the same sample size.

In semiconductor-type gas sensors, the surface and grain boundary was usually covered with adsorbed oxygen and water, therefore, the electronic conductivity of the semiconductor-type sample was related to these sorption radicals and their amounts on the region.

Studied found that the hydrogen detection sensitivity was consistent with the Schottky barrier height difference. High quality of Schottky contacts had been key factors in improving performance and reliability. Due to ionic character of the Ga-N bondings, no Fermi level pinning increase at the metal-GaN. Thus, the barrier height of metal contacts to GaN 54ncreased with the metal work function Φ_m . Metals such as Pt (Φ_m = 5.65 eV) and Pd (Φ_m = 5.12 eV) were commonly used for Schottky contacts to n-GaN.

These metals were useful for contacts because of its resistance to oxidation and corrosion. According to J. Wang et al [13], the Schottky barrier heights of Pt/n-GaN decreased greatly after annealing above 600 ^{0}C. The GaN materials system appeared to be very promising for using in combustion gas detection, especially as part of integrated sensor structures that could also detect UV radiation.

4. CONCLUSION

In summary, the studied showed that the physical properties of the GaN samples changed after being etched to become porous layer. We can see that by increasing H_2 concentration, it showed an increase of the current, which can be attributed to a decreased in the Schottky barrier height. Porous GaN samples yield better sensitivity compared to the as grown samples in hydrogen gas sensing. With increasing hydrogen concentration, the sample of porous showed a rapid increase in $\Delta\o_B$ compare to as grown GaN sample. This positive hydrogen concentration dependence can be attributed to the increased collision among hydrogen atoms that induced higher reaction rate and more hydrogen atom trapped at the semiconductor interface. In a constant current operation mode, this reduction of the Schottky barrier height resulted in a shift to lower bias voltage, which constituted the sensor signal.

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