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Hexagon Platinum Schottky Contact with ZnO Thin Film for Hydrogen Sensing

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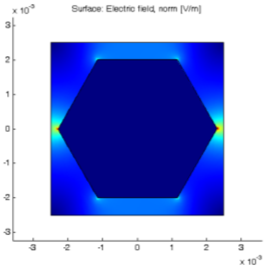
Graphical abstract



Abstract

This paper reports on the study of the effect on adding total peripheries and sharp edges to the Schottky contact as a hydrogen sensor. Schottky contact was successfully designed and fabricated as hexagon-shape. The contact was integrated together with zinc oxide thin film and tested towards 1% hydrogen gas. Simulations of the design were conducted using COMSOL Multiphysics to observe the electric field characteristic at the contact layer. The simulation results show higher electric field induced at sharp edges with 4.18×104 V/m. Current-voltage characteristic shows 0.27 V voltage shift at 40 µA biased current.

Keywords: Schottky diode; electrode; hexagon-shape; zinc Oxide; hydrogen sensor

Abstrak

Kertas ini membentangkan kajian tentang kesan penambahan jumlah sisi dan bucu tajam pada elektrod Schottky sebagai pengesan hidrogen. Reka bentuk dan fabrikasi elektrod-heksagon berjaya dilakukan. Elektrod tersebut digabungkan bersama lapisan nipis zink oksida dan diuji pada 1% gas hidrogen. Simulasi reka bentuk tersebut dilakukan menggunakan perisian COMSOL Multiphysics untuk memerhati sifat medan elektrik sekitar lapisan elektrod. Hasil simulasi menunjukkan bahawa medan elektrik yang lebih tinggi terhasil di kawasan berbucu tajam dengan magnitud 4.18×10^4 V/m. Ciri-ciri arus-voltan menunjukkan anjakan voltan sebanyak 0.27 V pada 40 µA pincang arus.

Kata kunci: Diod Schottky; elektrod; bentuk heksagon; zink oksida; pengesan hidrogen

■1.0 INTRODUCTION

Schottky diode has been reported to be used as a gas sensor besides from related devices such as MOSFET and Metal-insulator-semiconductor (MIS) structure. The incorporation of Schottky contact such as Platinum (Pt) or Palladium (Pd) which works as catalytic metal has been widely studied for hydrogen sensing application. The catalytic metals can dissociate molecular of hydrogen gas into atoms hence creating dipole charge at the metal-semiconductor interface thus changing the barrier height [1].

Hydrogen (H_2) as one of the potential renewable energy, trade off with its hazard of becoming explosive with concentration as low as four percent upon exposure to air [2]. It has broad applications in industries such as oil and gas, nuclear power plant, hydrogen cooled for generators and in laboratories. Therefore proper detection of H_2 needs a good sensitive sensor to avoid unwanted accident.

Nanostructured zinc oxide (ZnO) materials received interest with emerging nanotechnology. The advantage of using metal oxide is due to its chemical properties that have been utilized in sensors and transducers. Due to its flexibility in changing structure and size, it is widely studied to obtain higher sensitive sensor and showed promising results [3]. ZnO with a band gap of 3.37 eV allows the electron flow to be 'less restricted' since the energy dividing the valence band from the conduction band is large enough. Hence, current-voltage (I-V) characteristics becomes sensitively more conductive [4].

ZnO has been reported to be used as hydrogen sensor with better response after combined with Pt or Pd [5]. Previous reports proved that the sharp edges which were induced by nanostructures enhance the sensitivity of hydrogen sensor by lowering the barrier height. It is described that enhancement of the electric field around the sharp edges of nanostructures gave prominent changes in reverse biased mode. This is due to increment of current density at reverse biased mode is a strong function of summation of ambient and localized electric field at the corners and sharp edges of the nanostructures [1]. In this paper we have studied the effects of adding sharp edges to the Schottky contact layer instead of nanostructure and its application as hydrogen sensor.

Configuration of this sensor is as shown in Figure 1. This type of configuration had also been tested towards ethanol vapor but gold material was used instead of platinum and it shown a remarkable response in sensing[6].

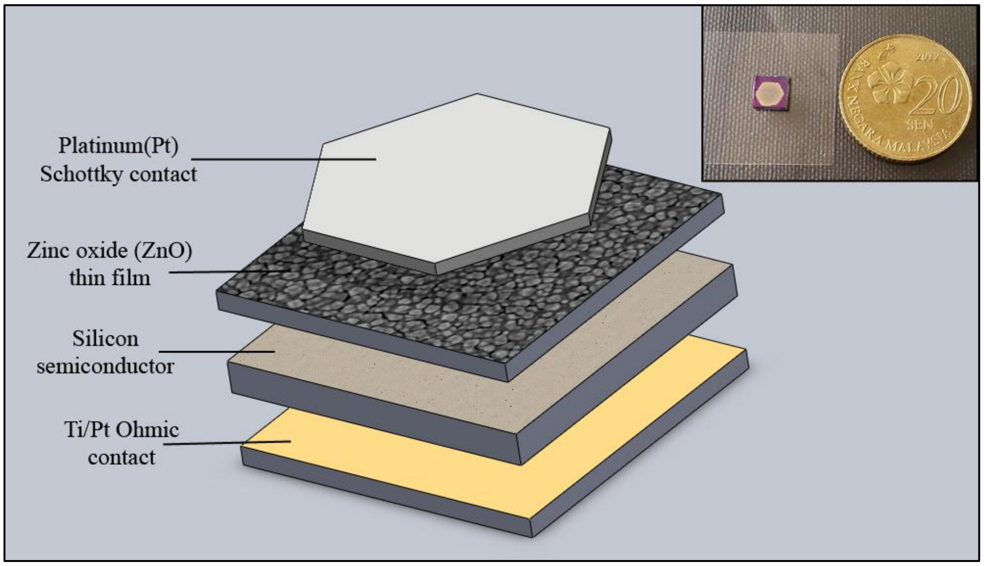


Figure 1 Configuration of vertical Schottky diode layers. Inset: Real picture of the fabricated device compared with the size of twenty-cents coin

■2.0 EXPERIMENTAL

2.1 Simulation

To validate the effect of adding edges to the Schottky contact, simulations were conducted by using COMSOL Multiphysics. Hexagon-shape was designed and simulated. The design for the contact was based on the circular shape with 4 mm diameter. The area for this model is 13.86 mm^2 . The dimension of substrate is 5 mm x 5 mm squares based on the fabricated Schottky diode sensor. Electric potential of 5 V was applied at the Schottky contact layer.

2.2 Fabrication

Zinc oxide Schottky diode hydrogen sensor was fabricated using n-type silicon wafer. Silicon wafer was cut into smaller pieces with the dimension of 5 mm x 5 mm using a diamond cutter. It was then cleaned with hydrofluoric acid (HF) and rinsed with deionized (DI) water to remove any oxide grown on the substrate. ZnO thin film was obtained by depositing 99.9% zinc target (Nanorian Technologies) via RF sputtering method. Zinc was sputtered in 10 mTorr chamber pressure with 200 W RF power. ZnO film was obtained in an $Ar:O_2$ (4:1) mixture ambient for 60 minutes in 250 ˚C temperature.

Layer of metals Ti/Pt were then coated on the unpolished side of silicon as back contact. Platinum was sputter-coated on top of ZnO as the Schottky contact and catalyst using hard mask of hexagon shape. The contact was deposited using JEOL JFC-1600 AutoFine Coater for 300 seconds with thickness ~100 nm measured with surface profiler. In order to obtain the nano scale grain that increases the surface to volume ratio, the sensor then was further annealed in furnace for 30 minutes in 500 ˚C temperature [7]. It also conducted to form ohmic contact at Ti/Pt layer.

The surface morphology of the deposited film was observed using Field Emission Scanning Electron Microscopy (FESEM). The thickness of the thin film was measured using the surface profiler. For gas sensing performance, sample was measured using Keithley 2400 sourcemeter to obtain the current-voltage characteristics. Series of different temperature varying from room temperature to 200 ˚C were tested to observe the highest voltage shift for the fabricated sensors. Measurement were conducted in a vacuum chamber flow with carrier air and purged with 1% hydrogen as the target gas. The concentration of the hydrogen was controlled by mass flow controller (MFC) and fixed at 90 sccm through experiments. Figure 2 shows the setup of the gas sensing equipments.

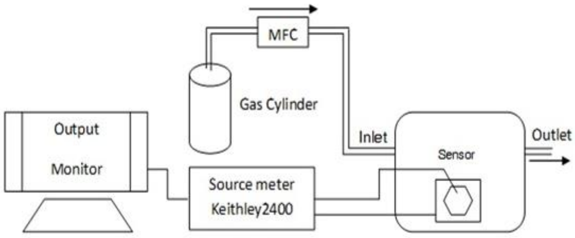


Figure 2 Gas sensing measurement setup

3.0 RESULTS AND DISCUSSION

3.1 Electric Field Simulation

Electric field distribution of the hexagon-shape Schottky contact was shown in Figure 3. Longer arrows indicate higher level of electric field at the surface whereas shorter arrows show the weaker level of electric field.

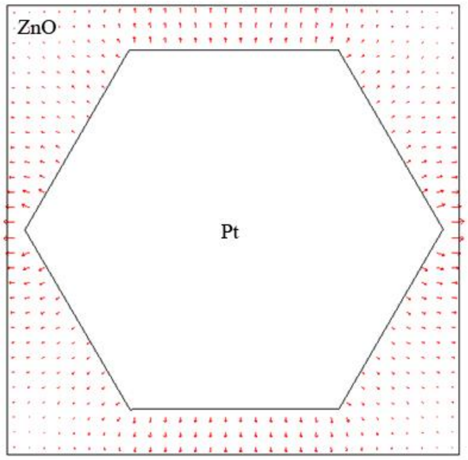


Figure 3 Arrow showing distribution of electric field on hexagon-shape Schottky contact

It is well noted that electric field is higher when closer to the edges of the substrate. It is observed gradually decrease by distance from the contact. This is due to the accumulated charges at the sharp points of the hexagon [8].

Figure 4 illustrates the magnitude of electric field based on the hot color scales. It is observed that the magnitude is not uniformed at every edge but was highest when it was closer to the substrate edge (left and right side of hexagon-shape). From the simulation the highest peak magnitude of electric field is $4.18 \times 10^4 V/m$.

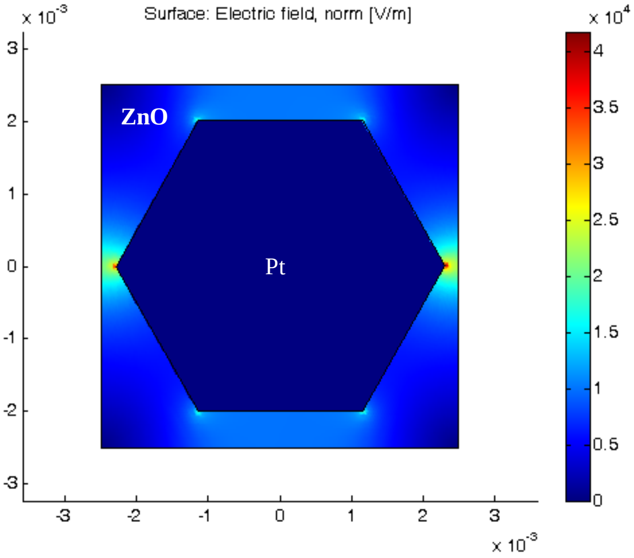


Figure 4 The electric field level on hexagon-shape Schottky contact

3.2 Physical Characterization

Figure 5 presents the captured image from FESEM of a ZnO thin film. It shows the pack grains of ZnO nanostructures. The average size of the nano-grains is ~21 nm in diameter. The pack nanostructure grains on the film improve the surface to volume ratio for hydrogen adsorption during sensing operation. The thickness of the thin film is ~0.44 µm and was obtained using surface profiler.

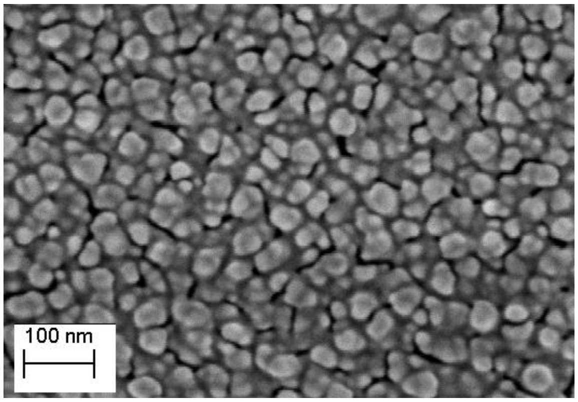


Figure 5 SEM image of ZnO thin film

3.3 Electrical Characterization

Series of current-voltage (I-V) characteristics of hexagon Pt/ZnO/Si Schottky diode were observed by using Keithley 2400 sourcemeter. Fig. 6 shows the barrier height, ϕ_B obtained by using Eqs. 1. In which k is Boltzmann constant, T is temperature, q is charge, A is Schottky contact area, I_o is current density and A^{**} is Richardson constant of ZnO which is 32 cm^{-2} K^{-2}.

The barrier height changes with the increasing temperature and current still capable to surpass through the barrier at high temperature although the barrier height is higher. This is plausible due to more energy was obtained in high temperature and high level of catalytic activity takes place for H_2 dissociation. ϕ_B calculated from Eqs. 1 is 0.695 eV at room temperature. It can be calculated after obtaining the current density from the *ln* graph.

$$\emptyset_B = \frac{kT}{q}\ln\left[A.A^{**}.\frac{T^2}{I_o}\right] \qquad (1)$$

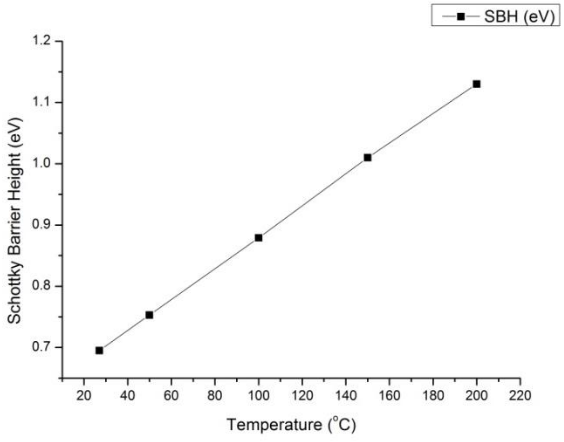


Figure 6 Schottky barrier height increasing with temperature

Figure 7 illustrates the I-V characteristics of this sensor. The diode shows good rectifying characteristic at forward biased and breakdown at reverse biased. Lateral voltage shift was seen after exposed to hydrogen.

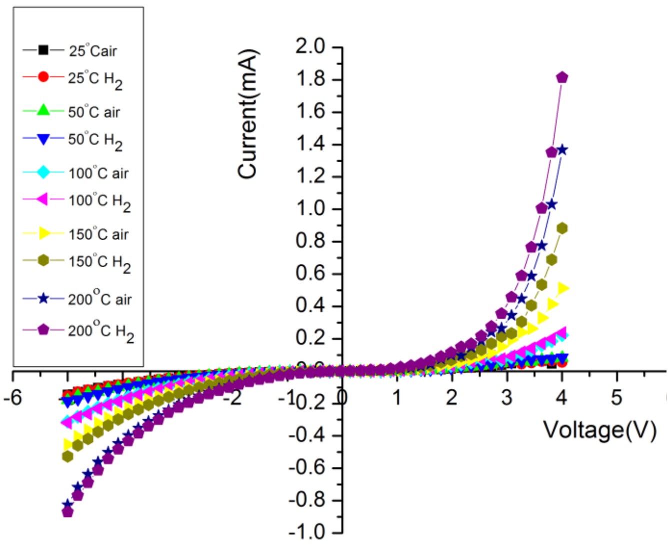


Figure 7 I-V characteristic of hexagon Pt/ZnO/Si Schottky diode sensor towards 1% hydrogen at different temperature from 25°C to 200°C

Table 1 summarized the voltage shift extracted from the I-V characteristics at constant current of 30 and 40 µA. From the I-V characteristic in Figure 7, the differences of the voltage shift revealed that the optimal temperature for this sensor to operate was at 150 °C. It is interesting to note that the voltage shift was higher in forward biased mode compared to the reverse biased mode despite the enhancement of electric field at Schottky contact. This can be justified from the grain of ZnO nanostructures which does not have sharp edges morphology such as nano-wire or nano-platelets [9].

From this observation, it can be assumed that a uniformed high electric field was needed in order to observe high voltage shift in reverse biased mode. The non-uniformed high electric field at hexagon Schottky contact would probably only allow such area to have thermionic current transport at high magnitude of reverse biased voltage. On the other hand, the sharp edge of nanostructured thin film provides the platform of a uniformed high electric field. This advantage assists the current transport since barrier height is a function that is dependent on area. This remarks that larger area of high electric field lowered the barrier height. Therefore, the current density at reverse biased mode was increased. Nonetheless this sensor still shows a good response towards H_2 at forward biased with 0.27 V voltage shift at 150 °C.

Table 1 Voltage shift measured at forward and reverse biased

	Voltage Shift, ΔV (V)			
	Forward Biased		Reverse Biased	
Current (µA) / Temperature (°C)	30	40	-30	-40
25	0.23	0.17	0.03	0.00
50	0.17	0.12	0.06	0.06
100	0.04	0.07	0.03	0.03
150	0.27	0.27	0.15	0.14
200	0.25	0.23	0.07	0.10

■4.0 CONCLUSION

From the comparison made between the distribution and the magnitude of electric field, it can be concluded that the sharp edges of Schottky contact provides higher electric field level especially near the sharp edges thus giving a non-uniformed magnitude of electric field across the surface. The performance of high electric field was demonstrated in an experiment in which Pt/ZnO/Si Schottky diode with hexagon Schottky contact shapes was fabricated and tested towards 1% H_2 gas. Schottky barrier height calculated was 0.695 eV at room temperature. The largest voltage shift was observed in forward biased mode with 0.27 V measured at 40 µA constant biased current. It is believed that the adsorption process in the sensing mechanism could be improved after combining it with a better morphology of nanostructure. Sharp edges morphology such as nano-wire or nano-platlets is preferred and will be added in future works.

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