International Journal of Information, Control and Computer Sciences
ISSN: 2517-9942
Vol:7, No:6, 2013

High Temperature Hydrogen Sensors Based On Pd/Ta_2O_5/SiC MOS Capacitor

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Abstract**—**There are a many of needs for the development of SiC-based hydrogen sensor for harsh environment applications. We fabricated and investigated Pd/Ta_2O_5/SiC-based hydrogen sensors with MOS capacitor structure for high temperature process monitoring and leak detection applications in such automotive, chemical and petroleum industries as well as direct monitoring of combustion processes. In this work, we used silicon carbide (SiC) as a substrate to replace silicon which operating temperatures are limited to below 200°C. Tantalum oxide was investigated as dielectric layer which has high permeability for hydrogen gas and high dielectric permittivity, compared with silicon dioxide or silicon nitride. Then, electrical response properties, such as I-V curve and dependence of capacitance on hydrogen concentrations were analyzed in the temperature ranges of room temperature to 500°C for performance evaluation of the sensor.

Keywords**—**High temperature, hydrogen sensor, SiC, Ta_2O_5 dielectric layer.

I. INTRODUCTION

VARIOUS gas-sensing elements have been developed for the detection of numerous target gases [1], [2]. Among them, metal-oxide semiconductors [3], [4] have been considered as typical elements for gas sensing because of their good sensitivity and reliability. Most metal-oxide semiconductor gas sensors are based on the principle that when the sensor reacts with specific gas molecules, the surface of the sensor undergoes certain changes, which in turn result in changes in the electrical properties of the sensor, such as its resistance or capacitance. These sensors usually operate at an elevated temperature for maximum performance.

Today hydrogen has many important applications such as its use in the processes of many industries that include chemical, petroleum, food and semiconductor. Furthermore, the negative environmental impacts of burning fossil fuels, coupled with rising oil prices, have led to renewed interest in clean energy technologies, especially those involving hydrogen. But, there are some obstacles to fulfill its potential as a fuel source because of hydrogen's safety. By nature, hydrogen is explosive and its low mass and high diffusivity makes it difficult to store. If hydrogen flows into the air from a tank or valve, it will pose hazardous. Therefore, it is of great attention for detection of hydrogen leakage, which is below the lower explosive limit of 4% by volume ratio of hydrogen to air. Hydrogen is also a major cause of corrosion. This happens when tiny hydrogen atoms penetrate into steel and other metals and deteriorates the metals internally, which results in hydrogen blistering or hydrogen embrittlement where properties of metals, such as durability, strength and fracture toughness, are affected. This is especially deteriorated at elevated temperature.

Currently, hydrogen sensors [5]-[8] have been demanded widely as essential components in industries such as glass, chemical and petroleum industries that require storage tanks and refining process, where the leakage of hydrogen is unavoidable. Besides, hydrogen sensors may be necessary for direct monitoring of processes which may require them to be placed in high temperature environments where temperatures may exceed 500°C.Temperature of automotive exhaust parts for cylinder specific combustion rises to 700°C, but there are a few of devices capable to operating at this high temperature. Hence, devices as well as materials and sensing structures capable of withstanding such conditions should be exhaustively investigated.

By the way, silicon has been widely used as a substrate for semiconductor devices as it is widely available and has an established technology in electronic processing and packaging. Nevertheless, due to its narrow bandgap, the operating temperature of Si is limited to below 250°C, resulting in restricting its use to specific high temperature environments. If Si-based electronic devices operate at ambient temperature above 250°C, it can lead to disorder as self-heating at high power levels results in high internal-junction temperature increase and leakages.

SiC has emerged as the leading candidate substrate for field effect based sensors which are suitable to high temperature operation [9]-[11]. As well as its compatibility with Si, its wide band gap, chemical inertness and stability have made it still more ideal for this object. Furthermore, SiC substrate is commercially available, it has known device processing techniques and it has an excellent ability to grow a good quality of thermal oxides. As a result, SiC is now in the forefront of wide bandgap semiconductor research. Generally wide-bandgap semiconductors allow high temperature operation up to 1000°C. This property of SiC allows hydrogen

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sensors based on this material to be integrated with high-temperature electronic devices on the same chip. Moreover, it has excellent thermal conductivity (3~4.9W/cmK), chemical inertness and radiation hardness. This unique quality offers the chance to eliminate or at least minimize the expensive bulky cooling systems that protect electronic devices from harsh environments. Consequently, it is sure that SiC-based hydrogen sensor can operate well at high temperature.

In this work, tantalum oxide (Ta_2O_5) was investigated as a dielectric material. For high temperature applications, the effective choice of dielectric material in SiC-based hydrogen sensors is important since dielectric layer allows MOS capacitors to operate at temperatures in excess of 900°C by separating metal electrode from SiC. Tantalum oxide [12] has been recognized as an attractive material in applications such as coating, catalysts, electronic circuit system and it is best utilized in capacitors due to its high-κ dielectric. It has also been reported as very promising candidate for sensor applications of a capacitor type.

In this work, we demonstrate a hydrogen sensor fabricated into a MOS capacitor which consists of tantalum oxide layer deposited on SiC substrate for high temperature applications.

II. Experimental

A. Device Fabrication

To fabricate hydrogen sensors of a MOS capacitor, we used 4H-SiC wafers as substrates. The application of 4H-SiC wafers is usually suitable to electronic devices. Currently, 4H-SiC electronic devices are the most promising due to the availability and quality of reproducible single-crystal wafers, compared to other polytype of SiC substrates. In addition, its wide bandgap dramatically reduces the number of electron-hole pairs formed from thermal activation across the bandgap, which allows high temperature operation of SiC electronic devices including sensor.

After cleaning samples, tantalum was sputtered on SiC substrates of $1cm^2$ area for 2min in power of 300W, where oxidation of tantalum was followed by exposing the tantalum metal to an atmosphere containing oxygen by rapid thermal processing (RTP) at 500°C for 3min. Under the controlled oxidation condition, thermally grown tantalum oxide was found to be very reproducible and very stable chemically. After the oxidation, Ni was deposited as back-side electrode by sputtering for 20min in power of 300W, followed by RTP at 950°C for 1min to stabilize Ni electrode. Next, Pd was deposited on Ta_2O_5 tin film with a shadow mask. Choice of catalytic metals depends on the nature of the gas to be detected. In this work, Pd metal electrode is used as a catalyst for the chemisorption of hydrogen on the surface with regard to the dissociation of hydrogen molecules because it has been known that Pd has much higher solubility of hydrogen than Ni and Pt and that the diffusion of hydrogen through Pd is very fast. The adsorption of hydrogen in metal depends on temperature and hydrogen concentration.

Our hydrogen sensor, as shown in Fig. 1, was fabricated into a SiC-based MOS capacitor with Ta_2O_5 dielectric layer of 80nm thickness and a Pd electrode of 200nm thickness and 5mm diameter.

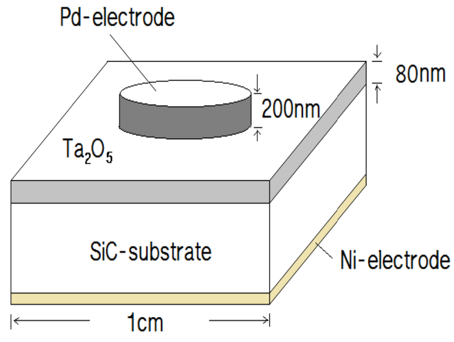

Fig. 1 Schematic diagram of the hydrogen sensor

B. Measurements

Electrical measurements for sensors were carried out with a semiconductor device analyzer and a LCR meter. The sensors were measured in a chamber which can control the temperature from 150 to 900°C. The chamber was composed of a quartz tube of 75mm diameter with cooling system. We injected hydrogen gas through a hydrogen MFC (mass flow controller). Hydrogen concentrations in a chamber were varied up to 2,000ppm in temperature ranges from room temperature to 500°C. The sensors were flushed with clean nitrogen gas before exposure to hydrogen gas. Fig. 2 shows a set of equipment for testing our hydrogen gas sensors.

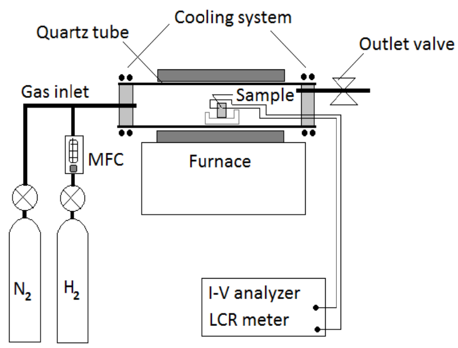

Fig. 2 A set of equipment for testing hydrogen sensors

III. Results and Discussion

A MOS-capacitor sensor is the simplest MOS device with a catalytic metal electrode. This device is very sensitive to low gas concentration and it has a simple and compact structure that can be economically mass-produced via microelectronic fabrication techniques. Such devices are attractive due to their chemical specificity and high sensitivity to specific gases. They can operate at elevated temperature with high degrees of sensitivity and selectivity. Besides, they are very simple to fabricate, which are extremely suitable for sensor array integration.

Electronic or physical properties of the sandwiching dielectric layer in devices mainly determine whether the behavior of a device is a diode-type or a capacitor-type. For a capacitor-type response, the dielectric layer must be a good insulator, which capable of providing a huge tunneling barrier for the carriers. Generally, devices that have dielectric layer of 50nm thickness may be grouped in MOS capacitor or Schottky diode according to their working principle. In this work, we were able to demonstrate that our Pd/Ta_2O_5/SiC sensor could operate in dual mode either as a rectifying diode or a capacitor, where Ta_2O_5 thickness was about 80nm. Fig.3 shows a current-voltage (I-V) curve measured in the sensor under applied static voltage from 0 to 5V at room temperature without any hydrogen injection. Even though the sensor was fabricated as a capacitor-type, it indicated rectifying characteristics where the turn-on voltage was around 2V.

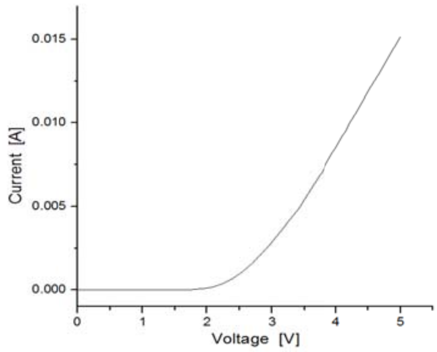

Fig. 3 I-V curve observed at room temperature

For a MOS device to operate as an ideal capacitor which terminals are placed on the catalytic metal and SiC substrate, the oxide layer thickness is typically larger than for the diode's, around 100nm, which is to prevent tunneling between the metal and semiconductor substrate. Furthermore, this oxide layer must be insulating in order to prevent current conduction and to facilitate the buildup of charge on either of its sides. In this MOS capacitor, the total capacitance is given by the series addition of the oxide and semiconductor capacitance, C_{OX} and C_S, respectively, and is expressed by

$$C_{TOTAL} = \frac{C_{OX}\, C_S}{C_{OX}+C_S} \qquad (1)$$

Fig. 4 shows the variation of capacitance on exposed hydrogen concentrations as a function of temperatures from room temperature to 500°C. In this experiment, hydrogen concentrations were varied from zero to 2,000ppm by the step of 500ppm. We observed the dependence of capacitance on hydrogen concentrations. As the result, at room temperature the capacitances in the samples were nearly invariable regardless of hydrogen concentrations, but at high temperature above 150°C the capacitance changed high for the hydrogen concentrations with the increase of temperature up to 500°C. Especially, the slope of the variation was indicated relatively higher in the low hydrogen concentration range of 500ppm than in the high hydrogen concentration range of 2,000ppm. Therefore the sensor showed a possibility detectable to even low concentrations below 500ppm.

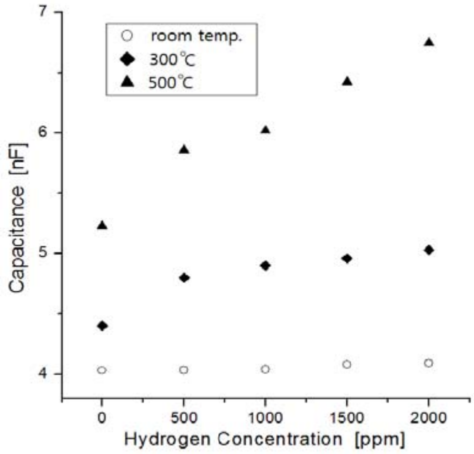

Fig. 4 Dependence of capacitance on hydrogen concentrations as a function of temperature

For harsh environment applications, the operating temperature of SiC-based MOS capacitor hydrogen sensors should be higher than 150°C at least. Fortunately, the time response of the sensor can be sped up at elevated temperatures and the sensitivity can be improved because the diffusion of hydrogen molecules to dielectric layer is fast as well as the sticking of water molecules to the metal surface is prevented. We found that the response time was shortened with increasing temperatures, as expected. Fig. 5 shows a response behavior when 500ppm hydrogen gas was surrounded to the sensor at 500°C. The capacitance increased rapidly from 5.3nF and was saturated near to 5.8nF after 30second lapse. Consequently, the hydrogen sensor showed fast response properties.

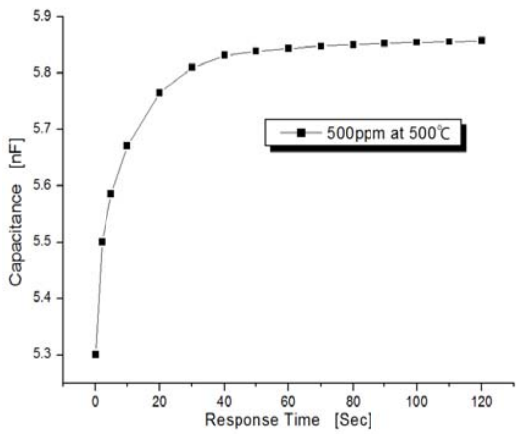

Fig. 5 Response behavior of the sensor at 500ppm hydrogen ambience

IV. Conclusion

As chemical sensors based on Si substrates have operating temperatures limited to below 200°C, the growing need for development of high temperature operation sensors has been raised to solve this problem. Currently, SiC-based sensors appear to be the strongest candidate to replace Si-based sensors for harsh environment applications which are related to automotive, aerospace, avionics, micro-propulsion, nuclear power and well-logging industries. The development of hydrogen sensors based on SiC is a representative example. In this work, we developed a SiC-based hydrogen sensor operating at high temperatures above 300°C, low hydrogen concentrations below 500ppm. Our sensor consisted of Ta_2O_5 dielectric layer deposited on SiC substrate with Pd electrode as catalyst. As the result, the variation of capacitance in the sensor was observed very extensively in low hydrogen concentration ranges of hundreds of ppms with increasing temperature up to 500°C. Therefore the sensor showed promising performance for hydrogen detection at high temperature.

Acknowledgment

This research was financially supported by the Ministry of Education, Science Technology (MEST) and National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation.

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