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Catalytic Pd–TiO_2 thin film based fire detector to operate at room temperature

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ABSTRACT

Attempts made in past to detect target gases using semiconductor structure required high operational temperature. Whereas, in the present study, our research group could detect CO_2 gas at room temperature without using vacuum condition. For this purpose, a micro-fabricated device was made with simple MIS structure having Pd/TiO_2/SiO_2/Si-wafer/Al layers. The sensing performance of device was dependant on Pd–TiO_2 catalytic sensing layer quality because the role of TiO_2 layer was to reduce work function barrier between palladium and SiO_2 layer. The TiO_2 layer prepared by sintering at 500 °C or above showed anatase phase in XRD analysis. By using this device we could detect between 2.5% and 12.5% CO_2.

1. Introduction

Fire detectors are essential equipment at places like hospitals, offices, school and living quarters. Attempts made in past to develop fire alarm [1] suffered drawbacks in terms of sensing performances, for example, requirement of high concentration of CO_2 and high operational temperature (50–400 °C). Additionally, a fire sensors needs to be rapid and accurate. Therefore, in the present study we made an attempt to develop CO_2 gas sensor operable at room temperature. The configuration of this sensor adopts a catalytic-metal-insulator-semiconductor (MIS) structure. Catalytic Pd–TiO_2 thin film was used as a gas sensing layer because of its known ability to detect volatile organic compounds [2], including carbon dioxide (CO_2) gas at low operational temperature [3]. Also, Pd–TiO_2 is less expensive and toxic than commonly used sensing layer such as CdS, GaN, SnO_2, InO_3, etc to fabricate gas sensors [4] and Pd has higher catalytic action than typical catalysts Au and Pt [1,5].

The key mechanism of the sensor was based on the reactivity of Pd–TiO_2 film with CO_2. The CO_2 gas molecules are adsorbed on the Pd surface and molecules are ionized into ions. Consequently, those ions diffuse through Pd and reaches metal-insulator interface. This phenomenon creates a dipole layer that changes the work function between the Pd and TiO_2. Therefore, for resistivity-voltage measurement with gas supply, the *R–V* curve changes due to the formation of the dipole layer. CO_2 gas is detected mainly due to the decrease in work function. Thus, the sensing performance of the device is closely related to surface morphology of sensing layer. Various attempts have been made in past to extend the sensing surface area in such devices using techniques like single walled carbon nano-tube (SWCNT), multi-walled carbon nano-tube (MWCNT) [3], nano-imprinting, etc. However, those attempts produced limited success for the reason that those devices required up to 10% CO_2 concentration to show any response [4]. Therefore, in the present work, we shall emphasize on surface characteristics of Pd–TiO_2 film for improvement of CO_2 gas sensor performance.

2. Experimental details

2.1. Fabrication

The catalytic MIS structure in Pd–TiO_2 thin film gas sensor was fabricated on a low resistivity p-type or n-type heavily doped Si as Pd/TiO_2/SiO_2/Si-substrate/Al layers to the size 1.3 × 1.3 cm^2 using the method described in the process flow diagram (Fig. 1). The silicon wafer was cleaned to remove native oxide layer with SPM (sulfuric-peroxide mixture)-cleaning and then, SiO_2 insulator layer was grown on heavily doped silicon substrate by wet oxidation. The SiO_2 layer thickness was kept to 100 nm as per our previous experience for having good performance of gas sensor device. The back side of silicon wafer was etched to form the ohmic contact using reactive ion etching. Subsequently, a TiO_2 layer was deposited over SiO_2 surface to 100 nm thickness. The processed device was sintered at optimized high temperature (500 °C) for 1 h for removing residual solution and to build-up anatase structure [6]. In subsequent step, Pd (palladium) was evaporated with thermal evaporator to 60–70 nm thickness. This step was crucial for

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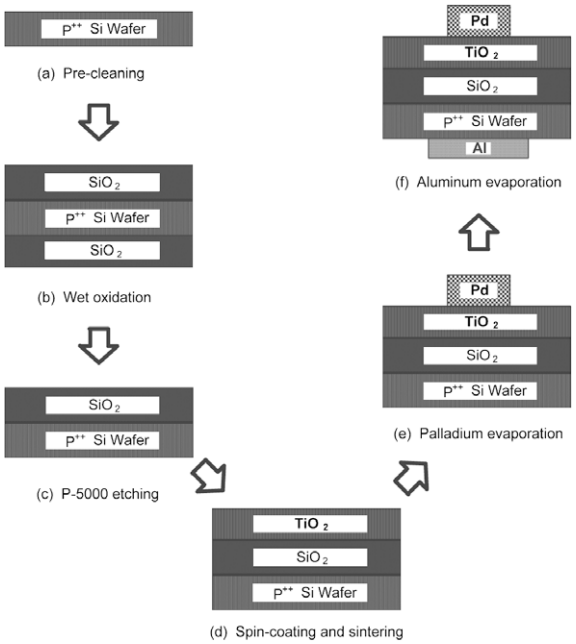

Fig. 1. Schematic diagram for fabrication of gas sensor device: (a) pre-cleaning of silicon wafer substrate, (b) SiO_2 deposited by wet oxidation, (c) back-side SiO_2 etching with P-5000 method (d) TiO_2 deposited with spin coater at 2000 rpm and sintering in 500 °C, (e) palladium deposited by thermal evaporation and (f) Al deposited by thermal evaporation.

the reason that surface roughness of Pd had direct effect on sensitivity of the device. Since Pd has high melting point, i.e. above 1500 °C, high current was applied for 600 s for the deposition. Finally, a metal Al contact, with thickness of 0.1 μm was evaporated at the opposite side of the device for an ohmic contact.

2.2. Spectroscopic and microscopic characterizations

Morphology of titania film was analyzed with atomic force microscopes (AFM, Parksystems, XE-100) using Pt–Ir coated SiN_3 tip under non-contact mode. The composition of the titania films was determined by a semiquantitative energy-dispersive X-ray (EDX, Hitachi, S-3500 N) analysis. The crystalline phase of titania films prepared under various conditions was determined using X-ray diffraction instrument. For this purpose, titania layer was prepared over ITO surface [6] at different sintering temperatures. The XRD diffractograms from these layers were compared with that from titania powder to analyze the possible presence of the peak related to the anatase phase. Field Emission Scanning Electron Microscope (FE-SEM) was also used for showing cross section of gas sensor device. For this purpose, the device was first coated with Pt and inserted in FE-SEM chamber under 10^{-5} torr vacuum.

2.3. Gas detection system

A gas chamber was designed with provision of gas flow through valves and ball flow meter, which could be controlled from 1 to 100 cc/min. The working volume of gas chamber was approximately 2 L. There were two gas flow lines with the chamber. One line was used for gas supply and the other line for collection of gas samples in a Tedlar® bag to confirm the concentration of gases with gas chromatography (GC) unit. Before injection of target gases, nitrogen was injected in chamber for removing other gases and making atmospheric condition (STP). The electronic interface of the detection unit had a Keithley® 236 voltage source and current measurement meter that could supply (−3 V) static and (−3 to 0 V) sweep voltages. In this study, static potential mode was used to determine the sensing time and the sweep voltage to obtain *I–V* curve.

3. Results and discussion

3.1. Analysis of TiO_2 film

Titanium dioxide (TiO_2) is well researched transition metal oxide. The increased interest in both the application and the fundamental research on this material in last few years is due to its remarkable optical and electronic properties [6–8]. TiO_2 also has good catalytic activity. Therefore, we analyzed the XRD patterns of TiO_2 film (Fig. 2), that shows the effect of sintering temperature on film formation. Only the TiO_2 layer prepared by sintering at 500 °C or above, showed the presence of anatase peak A(101). The result tallies with previous work related to TiO_2 phase [6] and also verifies earlier claim which correlates anatase phase with the sensitivity of gas sensor [5]. In other words, for getting the anatase A(101) peak of TiO_2, sintering temperature should be higher than 500 °C.

3.2. Analysis of palladium layer

The roughness of Pd layer which is deposited by thermal evaporation also affects the gas sensing performance in a similar manner as TiO_2. We examined the top view images of gas sensor device by AFM to ascertain its morphology (Fig. 3). It revealed the thickness of palladium as about 60 nm for 600 s deposition time. Thickness of palladium was kept at 60 nm and monitored by AFM. The surface roughness of Pd layer was evident from this AFM data. The AFM topography of palladium surface and cross section of gas sensor device was visualized by FE-SEM (Fig. 3), from which palladium layer structure could be seen and an estimate of particle size can be obtained.

3.3. Detection of CO_2 gas

For fire sensing application, we tried to measure CO_2 concentration using the fabricated device. A standard diagnostic test of the sensor operation was to sweep the voltage from negative to positive and measurement of the resistance. While using this diagnostics, devices showed typical Schottky diode *R–V* characteristics as previously reported by other group [5]. Before detecting carbon dioxide gas, experiment was performed under low vacuum and then with nitrogen gas. The injection of nitrogen into the gas chamber resulted in reduced output current of gas sensor. Subsequently, experiments were repeated with CO_2 gas and also with standard air. The sensing mechanism in this case was the reaction

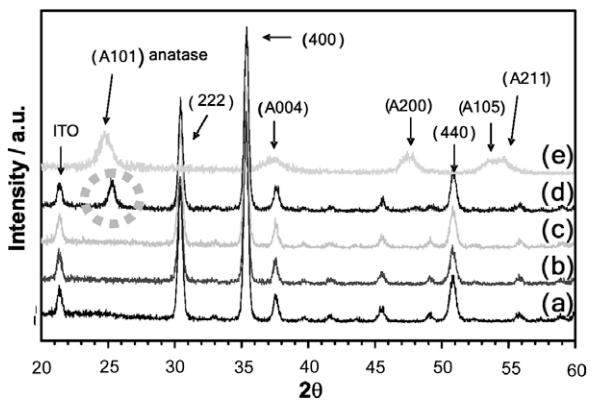

Fig. 2. XRD patterns of bare ITO (a) titania thin films prepared at various temperature for 1 h: (b) 150 °C, (c) 400 °C, (d) 500 °C and (e) TiO_2 powder.

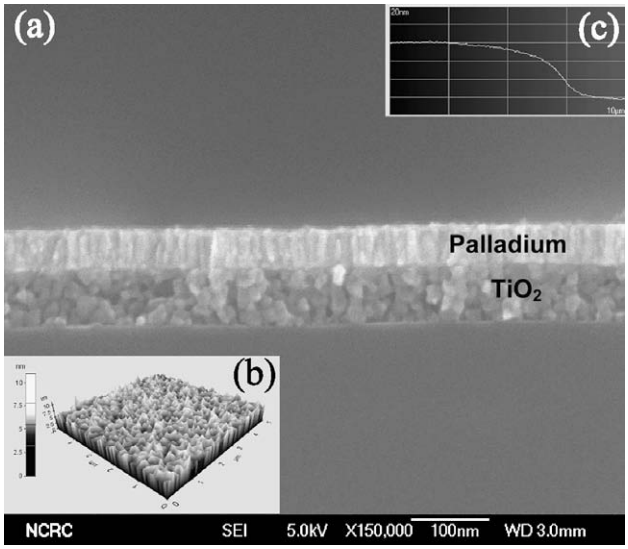

Fig. 3. (a) Cross sectional view of gas sensor device, (b) palladium surface monitored by AFM. (b) thickness of palladium, as measured by AFM.

of CO_2 with Pd–TiO_2 catalyst and thereby generation of ionic species (CO^-, O^{2-}, etc) which diffuse on the surface of Pd–TiO_2 and infiltrate into the TiO_2 layer. These ions change the work function between Pd and TiO_2 and resistance decreases due to presence of negative ions. The net decrease in resistance from baseline remains proportional to CO_2 concentration. Fig. 4 shows the increase in sensor response with respect to the carbon dioxide gas concentration ranging between 2.5% and 12.5%. As evident from this result, carbon dioxide concentration was directly proportional to sensor output. Also, the sensor performance was better as compared with previous reports in terms of operating temperature [9]. Our device could operate at room temperature and detect as low as 2.5% CO_2 concentration. The device sensitivity was much important criteria for fire detector application. The sensitivity of this device (S) can be given as (Eq. 1), where R is change of resistance from baseline.

$$S = R(\text{nitrogen})/R(\text{carbon dioxide}) \quad (1)$$

Upon plotting the sensitivity of device with respect to CO_2 concentration we yielded a linear correlation (Fig. 5). According to this result, when 2.5% of CO_2 gas was injected, sensitivity was about 3.72 while it was 3.91 with 12.5% of CO_2. This indicates that sensor

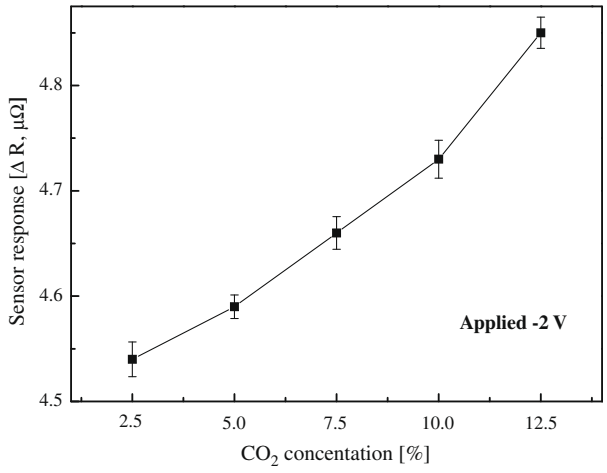

Fig. 4. Sensor response (ΔR) against CO_2 gas concentrations. The error bars represent standard deviation in triplicate measurements.

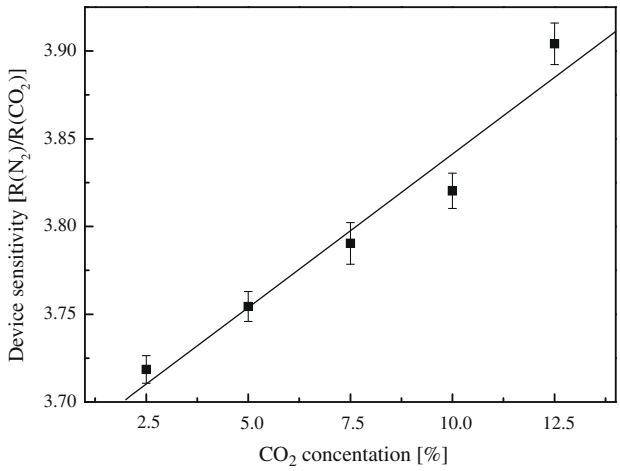

Fig. 5. Sensor sensitivity (R_2^N/R_2^{CO}) against CO_2 gas concentrations. The error bars represent standard deviation in triplicate measurements.

showed nearly equal sensitivity for entire detection range for CO_2. These results were important because all experiments were performed at room temperature and at low applied voltage unlike other groups (as much as 10 V) [10]. Therefore the fabricated device was power efficient and could detect CO_2 with high sensitivity.

4. Conclusion

A CO_2 gas sensor workable at room temperature was proposed using simple fabrication process. It had a silicon diode structure with palladium/TiO_2/SiO_2/heavily doped Si wafer/Al layers. It is proposed that CO_2 gas dissociates at the outer palladium surface, diffuses through the palladium film and is finally adsorbed at the inner palladium surface, thereby reducing the resistance of device. The gas sensing characteristics were investigated by measuring change in resistance with various concentrations of CO_2 gas. Under appropriate structural and operating conditions of the Pd/TiO_2 chemical sensor, identification and quantification of carbon dioxide was found feasible. Another advantage of this device was 2.5% as lower detection limit for CO_2 thereby eliminating the possibilities of false-alarm from smoking and kitchen related emission of CO_2. Therefore, our CO_2 sensor could be applied for fire sensor at various practical places.

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