SnO_2/Pt (40nm/10nm) Thin Films Sensitized for Enhanced H_2 Gas Sensing

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Received: May 31, 2019; Accepted: November 28, 2019

Abstract

Detection and alarm of leakage of hydrogen (H_2) gas is crucially important for safety use. In this study, we dedicate on the fabrication of H_2 gas sensors based on SnO_2 thin film sensitized with Pt islands. The H_2 gas sensors based on thin film of SnO_2 (40 nm) sensitized by Pt (10 nm) islands were deposited by reactive sputtering method using Sn, and Pt targets for the fabrication of sensor chips. The optimized sensor could be used for monitoring hydrogen gas at low concentrations of 25–250 ppm, with a linear dependence to H_2 concentration and a fast response and recovery time (2 – 35 seconds).

Keywords: SnO_2/Pt thin film, Gas sensors, H_2

1. Introduction

Hydrogen (H_2) is widely used in industrial applications for the synthesis of ammonia, petroleum and metal refining operations, hydrochloric acid production etc. H_2 is very explosive when it reacts with air in the range of volume 4% in air, which is at most important to monitor the H_2 leakage [1], [2]. Therefore, there has been a huge demand on effective gas sensor that can be used for detection and alarming of H_2 leakage during production, storage, transportation and usage. To monitor and precisely measure leakages, the development of a reliable sensor with improved sensitivity is crucial in preventing such fatal accidents [3]. Among a variety of semiconducting metal oxides, such as tin oxide (SnO_2) an n-type semiconductor is the most important material for gas sensor application because of SnO_2 exhibits high conductivity, good electrical stability and tunable crystal structure have been extensively used to sense H_2. However pure SnO_2 is sensitive towards many gases. So, H_2 sensor should be highly selective and sensitive to H_2 in order to minimize the accidents [4], [5].

For example, Gupta et al., has been made to study the catalytic role of different metallic clusters (Pt, Pd, Cr, Au, Cu, and In) hosted on the SnO_2 surface for enhance the sensing response such as H_2, NH_3, LPG, CH_4…[6]–[9]. Bizhou et al., using SiO_2 hollow microspheres and catalytic of Pt nanoparticales, showed a high sensitivity to H_2 [10] . Yin et al., show that the H_2 gas sensor based on the 1 at% Pt-SnO_2 exhibited high response, quick response-recovery time and high selectivity to H_2 against CO, CH_4, NO_2, and SO_2 [4]. The SnO_2 thin film can be generated using a variety of synthesis techniques including sputtering, sol-gel processing, spray pyrolysis, screen printing [11], [12]. Among these techniques, sputtering method is suitable for depositing thin film sensors uniformly, the thickness of the thin film is also controlled easily by the sputter conditions [13].

In this study, we describe about the response characteristics towards H_2 gas of activated SnO_2/Pt (40 nm/ 10nm) thin film sensor. It has been observed that Pt (10 nm) sensitized SnO_2 (40 nm) sensor exhibits a highest response (~4,6) at 400ºC for a concentration of 250 ppm hydrogen with a fast response and recovery time. The high performance of this sensor for the hydrogen sensing characteristic is attributed to the combined effect of spillover mechanism.

2. Experimental

Fig. 1 shows the design layout and sensor fabrication procedure of H_2 gas sensor based on Pt film-sensitized SnO_2 thin films (noted as SnO_2/Pt thin films). The sensor device comprises a microheater, a pair of electrodes using Pt/Cr layers deposited on a thermally oxidized silicon wafer, and a sensing layer of the SnO_2/Pt thin films as displayed in Fig. 1(A). A gas sensing layer of the SnO_2/Pt thin films was then patterned and deposited by reactive sputtering, followed by an ordinary sputter deposition. The 40nm thick SnO_2 thin film was deposited from a Sn target under the following conditions: based pressure of 10^{-6} Torr; working pressure of 5×10^{-3} Torr; and Ar/O_2 flow ratio of 50 : 50 [14]. Pt thin film with 10 nm thicknesses were deposited subsequently using a Pt as a target and sputter gases, respectively. Sputtering

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conditions were similar to that of the SnO_2 deposition. Namely, the deposition rate of Pt is 20 nm/min, thus by controlling the deposition time of 30 seconds, we could control the thickness of Pt thin film to be about 10 nm, respectively. The size of the sensing area was 150µm × 150µm, whereas the diameter and distance between the Pt islands were both 5 µm. The fabrication of sensor wafers involves the following processes as shown in Fig. 1(B): (1) - (2) thermal oxidation of Si wafer; (3) - (5) photolithography for the deposition of the Pt/Cr electrode and the microheater by sputtering; (6) lift-off; (7) – (11) patterned deposition of SnO_2 and Pt thin films as a sensing layer; (12) lift-off SnO_2/Pt thin film. Finally, heat treatment was conducted at 400°C for 2h in air to ensure the stability of the sensors.

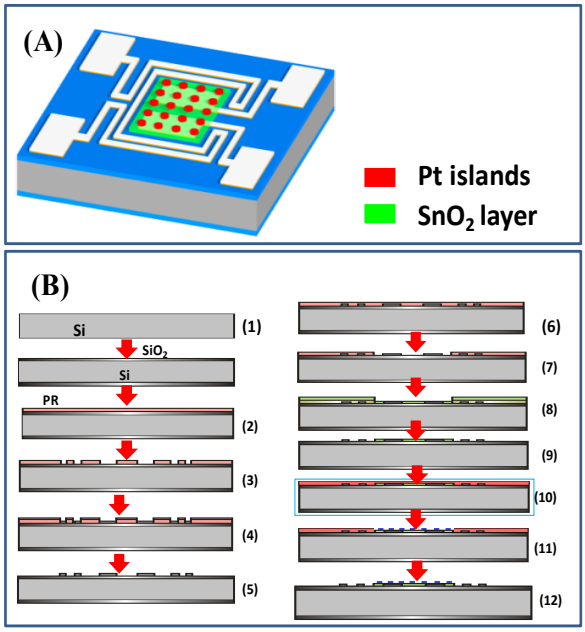

Fig. 1. Design layout (A) and sensor fabrication (B) Ref [14].

The morphology and the crystalline phase of the thin films and device shape were characterized observed by field emission scanning electron microscope (FESEM), X-ray diffraction analysis (XRD) and energy-dispersive X-ray spectroscopy (EDS) that was integrated in the FE-SEM instrument.

The gas sensing properties were measured in a dynamic flow system developed by iSensors group at International Training Institute of Material Science (ITIMS). A series of mass flow controller was used to control the injection of analytic gas into the sensing chamber. Prior to these measurements, dry air was blown through the sensing chamber until the desired stability of the sensor resistance was reached. Sensor resistance was continuously measured using a Keithley instrument (model 2602) that was connected to a computer while switching dried air and analytic gases on and off during each cycle. The total gas flow rate was 400 sccm. The sensor response to reduced gas is defined as $S=R_a/R_g$, where R_a and R_g are the resistances of the sensor in dry air and analytic gas, respectively. In this experiment, we used the standard gas concentration of 1 x 10^4 ppm H_2 balanced in nitrogen and mixed with dry air as carrier using a series of mass flow controllers to obtain a lower concentration. The gas concentration was calculated as follows:

$C(ppm) = C_{std}(ppm) \times f/(f+F)$, where f and F are the flow rates of analytic gas and dry air, respectively, and $C_{std}(ppm)$ is the concentration of the standard gas used in the experiment.

3. Results and discussion

Fig. 2(A) shows a SEM image of a representative fabricated sensor with the chip dimension of 4 × 4 mm. The sensor chip shows a defined SnO_2/Pt sensing area, which was surrounded by a 20 µm-wide meander wire heater. Fig. 2(B) displays a higher-magnification SEM image of the sensing thin film deposited on thermally oxidized silicon substrate. The thin film has a porous because of the polycrystalline nature of the oxide, which was obtained using the sputtering deposition method. The porous thin film composes of nanograins with an average size of less than 15 nm nanocrystals. The thickness of the SnO_2/Pt thin film is approximately 50 nm that by Profilermeter. To confirm the composition of the deposited thin film, the EDS data was recorded. Fig. 2(C) shows the EDS result presenting peaks of Pt, Sn, and O from the SnO_2/Pt sensing layer and Si from the substrate.

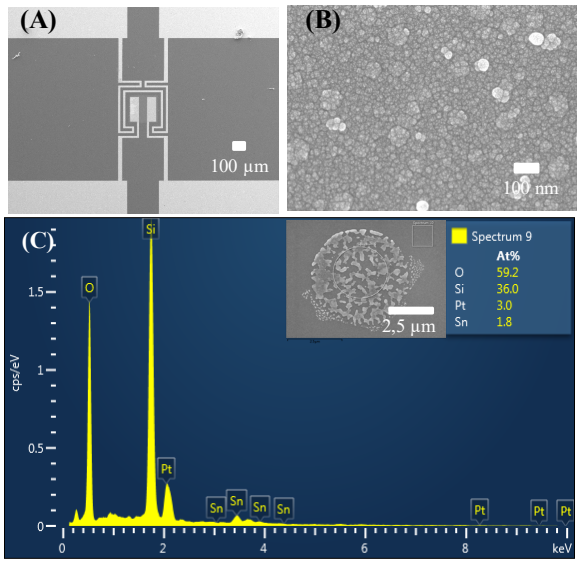

Fig. 2. SEM images of (A) a full chip, (B) SnO_2 thin film on SiO_2 and (C) EDS analysis of SnO_2 thin film sensitized with Pt islands.

Fig. 3 showed the response of sensor at various temperatures and concentrations of analytic gas. In all examined temperatures, the sensor respond decreased swiftly upon exposure to H_2 because of the natural behavior of an *n*-type semiconductor upon reducing gas. After refreshing the sensing chamber with dry air, the sensor respondse recovered rapidly to the initial values. This result indicated that SnO_2 thin film fabricated by sputtering method is relatively stable. The hydrogen gas sensing characteristics of the base SnO_2 thin film sensors were tested in different concentrations (100 - 250 ppm) of H_2 at temperatures of 300, 350, and 400◦C as in Fig. 3(A). The response of 250 ppm H_2 gas of SnO_2 thin film sensor nearly linear increased with increasing temperature (Fig. 3(B)). The respond value $S = 1,48$ respectively for 250 ppm at the temperature of 300°C.

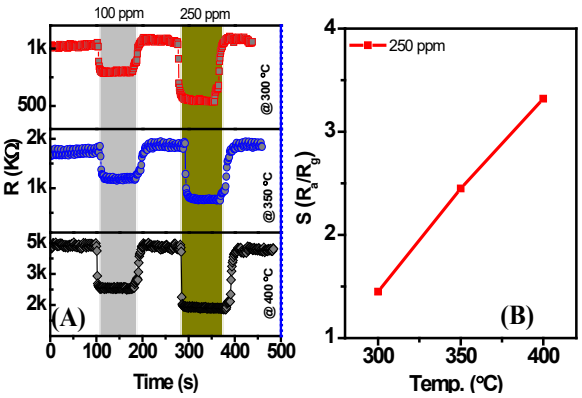

Fig. 3. (A) Transient response of bare SnO_2 and (B) Sensor response as a function of operating temperature.

That behavior was repeated when we increase the tested temperature to 350°C and 400°C and highest value is $S = 3,32$ at 400°C (Fig. 3(B)).

Our previous work [14], we choose the thickness of Pt islands 10 nm and the thickness of SnO_2 thin film at 40 nm to study the effect of Pt islands on sensor performance. Given that the SnO_2 thin film sensors that were sensitized with Pt islands have a superior sensitivity, thus low concentrations of H_2 (25 ÷ 250 ppm) were tested. The transient resistance vs. time upon exposure to various H_2 concentrations of the SnO_2/Pt sensors is shown in Fig. 4. At all measured temperatures from 200°C - 400°C, the fabricated sensors showed similar response characteristics to those of the bare SnO_2 thin film. This indicated that sensitization the SnO_2 thin film with Pt islands is much lower detection than the bare SnO_2. The sensors also showed linear response to very low concentrations of H_2 gas limit to 25 ppm H_2 (lower explosive limit of H_2 is 4%) but also in diagnosis of diseases through monitoring of hydrogen gas in exhaled breath. The response of the SnO_2/Pt sensor was 1,52, 1,78, 2,32 and 4,6 respectively for 25, 50, 100 and 250 ppm H_2 at the temperature of 200°C. The highest response of approximately $R_a/R_g = 4,93$ for 250 ppm at 400°C, it's more than higher the response of bare SnO_2. This sensor not only exhibited enhanced response but also functioned effectively at lower working temperature.

It is worth to note that in the report, where as the response to 300 ppm H_2 of nano-porous TiO_2-NiO film sensor reported by Kosc et al.. was only 2,46 at 300°C [15]. Shafiei, et al., investigated the barrier height changes for different concentrations of hydrogen gas which were obtained from the current-voltage (I-V) measurements of Pt/SnO_2. The respond to 5,000 ppm is 1,3 [10], [16].

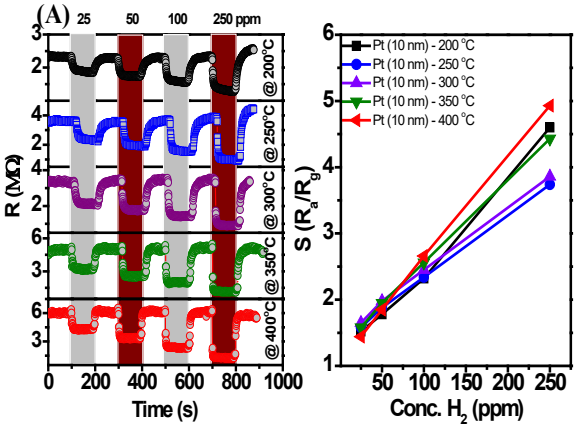

Fig. 4. Transient response of SnO_2/Pt (10 nm) island sensors (A). Sensors response as a function of gas concentration (B).

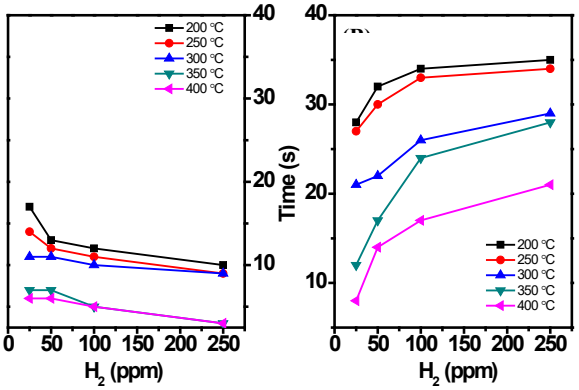

Fig. 5. (A) Respond and (B) Recovery time of SnO_2/Pt (10 nm) islands sensor.

Dhall S, et al., using combination of isolated Pd and SnO_2 nanoparticles on graphene shows improved sensitivity and good selectivity towards H_2 (S = 1,36 (13,6%) at 200°C, 2% H_2) and ethanol [17]. In the report by Rane et al., the response to 250 ppm H_2 (at 245°C) of a micro-sensor based on Pt/SnO_2 composite thin film was only 1,74 [18]. Duy et al., introduced the synthesis of undecorated and Pt decorated bead-like tin

oxide nanowires by a scalable and reliable method using Single-Walled Nanotube templates. The much higher responsivity of the Pt-decorated sample to H_2 compared with that of the undecorated one was possibly due to (i) the enhancement of the Shottky barriers between SnO_2 and Pt nanocrystals and (ii) the catalytic activity of Pt nanocrystals on the interactions between H_2 molecules and pre-adsorbed oxygen [19]..

The response and recovery times are two of the important characteristics of gas sensor. The time required attaining 90% of the stabilized value of sensor resistance (R_g) after exposing the target gas, which is called as the response time of the sensor, and the time required by the sensor to attain 90% of its original sensor resistance value after removing target gas (R_a) is referred to as the recovery time. The change of response and recovery times of the sensors measured at different temperatures was shown in (Fig. 5). For all temperatures, the response time was 2 - 35 second, and it took only 35 seconds for sensor to recovering initial stage. We can see that the response time is shorter than the recovery time, and they decreased with increasing of working temperatures. The result showed that the response-recovery speed of SnO_2 thin film sensor was fast enough for applications.

4. Conclusion

In conclusion, we have introduced the H_2 gas sensors based on SnO_2 (40 nm) thin film sensitized with Pt (10 nm) islands were successfully fabricated using microelectronic technique in combination between photolithography and sputtering methods. Gas-sensing characterization demonstrated enhanced H_2 sensing performance of SnO_2/Pt thin film. Experimental results have shown that these SnO_2/Pt sensors could detect low concentration of H_2 at ppm level with low working temperature of about 200 °C with good modulation for hydrogen gas and a response time as low as 2 seconds with the recovery time of 35 seconds. These characteristics suggest a possible use of this sensor for the early detection of hydrogen leakage and the monitoring of H_2 concentration in air.

Acknowledgments:

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.99-2018.16

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