A Sensing Properties Study On Miniature Au/SnO_2 Gas Sensor For Hydrogen Sulfide Detection

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ABSTRACT

The purpose of this study was to investigate the sensing properties for self-developed hydrogen sulfide gas sensor. In different temperature treatment and Au nano-particles doping ration, the sensitivity and selectivity of Au/SnO_2 gas sensor were optimized by observing the morphological, electrical and gas sensing properties. The results of experimental showed that on 400 °C firing temperature to fabricate SnO_2 sensing film, a linear dependence of the gas sensitivity on the resistivity of the sensor elements was found. The observed shift to higher gas sensitivities in comparison to sensors fired at 300 °C or 500 °C was caused by smaller crystallite sizes. The optimal crystallite sizes were 50 to 100 nm for improving the gas sensitivity significantly. Also for the doping ratio of Au nano-particles, the Au/SnO2 ratio at 1:100 was found that achieved an optimal sensitivity and selectivity, in this condition the detection range for hydrogen sulfide was about 0.2 to 20 ppm and could be operated at room temperature, and this self-developed gas sensor showed a good selectivity to avoid the interference of SO_2, NH_3, CO_2 or O_2. Even under the alcohol environment, we found there was no significant response to effect the hydrogen sulfide gas detection. However, we found to avoid the moisture interference that was important. Because the water molecules promote the electrical conduct on SnO_2 resistive sensing film that will significant interfere the target gas detection.

Keywords: gas sensor; tin oxide; hydrogen sulfide; Au nano-particles

1 INTRODUCTION

Hydrogen sulphide (H2S) is a colorless, toxic, corrosive and inflammable gas, is produced in sewage, coal mines, oil and natural gas industries, etc., and is utilized in many chemical industries. It has an occupational exposure limit of 10 ppm for 8 h exposure. Even at low concentration it produces severe effect on the nervous system, the health of peoples will cause some degree of damage [1], so it is necessary to prevent by the use of gas sensor, In the last few years, there were some reports about the sensors for hydrogen sulfide based on electrochemical means [2, 3] and metal oxides such as ZnO [4], and for nitrogen dioxide based on metal oxides or phthalocyanine compounds [5]. To improve the gas-sensing characteristics, semiconductor based gas sensors like SnO2, WO3 doped with Au, Ag, Cu, Zn or their composites are used. It is found that the doped or composite of SnO2 are prominent sensor material in the detection of several gases. The majority of the sensors showed a high response and good selectivity to H2S only at high temperatures with long response and recovery times [6]. In recent years, Research on tin dioxide (SnO2) based gas sensors continues to introduce sensors with better sensor response, time response and selectivity by focusing on the film composition and architecture including characteristics such as trace additives or dopants, film morphology, and surface treatments [7]. Among the SnO2 additives considered, gold (Au) has been demonstrated to dramatically improve tin dioxide gas sensors in terms of sensor response and selectivity to some target gases [8]. In the course of our studies of the interaction between H_2S and gold (Au) nano-particles, we find that the adsorption of H_2S molecules onto the nano-particles may significantly change the hopping behavior of electrons through the particles. Therefore, in this study, we used sol-gel method to prepare the tin oxide material with different ratios of Au nano-particles to quantify the level of H_2S gas, and analyzed the interference of sulfide dioxide, ammonia and carbon dioxide in sensing. Moreover, the gas sensing properties of thick film sensors were investigated to NH_2, H_2S CO_2, O2 and SO_2 at room temperature.

2 MATERIAL AND METHODS

In this study, the substrates material of we used is alumina which made from Wei Industrial Co., Ltd. in Taiwan, the dimension is thickness size 0.1 mm, length 10 mm, a width of 5 mm (**Fig. 1**). We used the method of spin coating for thin film fabrication of tin oxide. before the spin coating, the process is first to clean the impurities on surface and then we used the sol-gel method to prepare tin oxide sensing film, the tin tetrachloride ($SnCl_4 \bullet 5H_2O$) was dissolved in 70% alcohol, followed by adding and mixing the citric acid and ethylene glycol at 40 □ until the solution presented clear and transparent. Second, we put the solution into a 60 □ oven and waited for three days for gel to aging. Finally, the aged gel was cooled at room temperature to form a stable sensing film; in the meanwhile we also mixed different ratio Au nanoparticles into the aged gel. The ratio of SnO_2 and Au was doping in 100:1,100:5 and 100:10, respectively. The tin oxide gel was spin-coated on interdigital electrode by 2,000 rpm, and then was placed in a drying oven at 120 □ for six hours, after then, put it into the 400 □ calcination furnace by 10 □/min heating rate, and stopped at 400 □ for one hour to form SnO_2 films or SnO_2/Au films. The change of film resistance was recorded by a multi-functional digital meter (SEINTEK B4100) before and after gas sensing. Tested gas concentration was diluted by a gas calibrator (TELEDYNE Dynamic Dilution Calibrator Model 700) to control individual gas flows, Gas sensing sensitivity is defined as: $S = (| R_g - R_a | / R_a)*100\%$, where R_a is the sensor resistance in air, R_g is the resistance in tested gas.

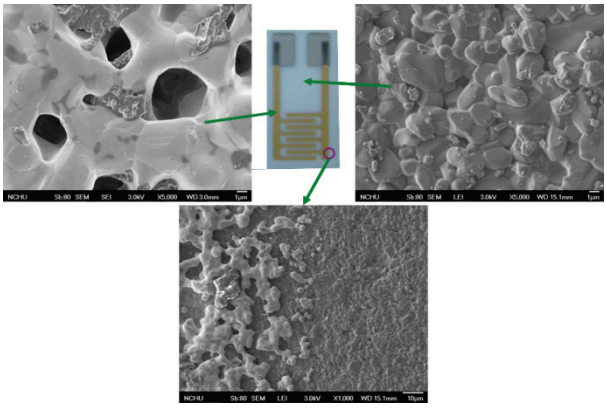

Figure 1: The SEM images of SnO_2 substrate without Au doping on inter-digital electrode.

3. RESULTS AND DISCUSSION

3.1 Response of hydrogen sulfide sensor

SnO2 is one of the most common used materials in the field of gas sensors and shows good sensitivity towards the detection of large variety of gases such as CO2, SO2, H2S, and NH3. The gas sensing mechanism is: when oxidizing agent is present, it extracts electrons from SnO2 material thereby decreasing its conductivity, while when reducing agent is present, electrons are injected into the SnO2 material and increasing conductivity. The surface of the SnO2/Au layer of the bi-layer films was exposited to the 1 ppm H2S gas, the response curve of electric signal is shown in **Fig. 2**. It took for 20 mins down to a steady state. The response time is too longer for practicing, so we shortened the measuring time to 5 mins to get a reasonable response rate.

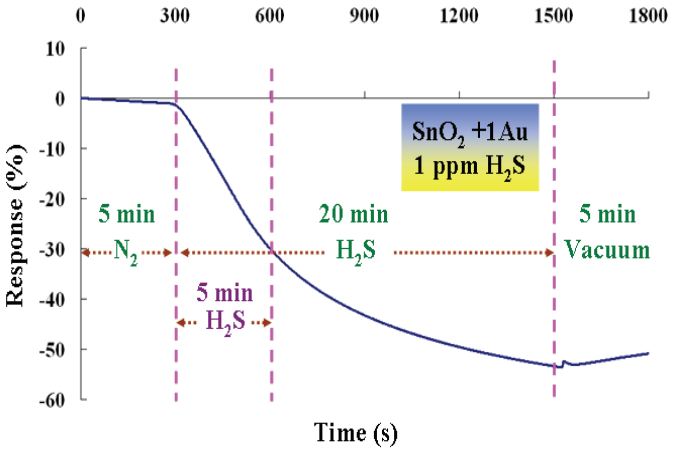

Figure 2: Response curve of Au-SnO2 sensor for H2S sensing.

3.2 Calibration curve of H2S sensor

Fig. 3 is the response curve to different Au doping effect, here we can find the optimized response that occurred in 1Au doping. We used this doping ration to do the following calibration curve. The **Figure 4** shows the calibration curve for H_2S detection on different ration of Au doping. We can find the best sensitivity is SnO_2/1Au, if we increase the doping ration of Au particles; the sensitivity looks not good enough. This self developing sensor it can detect low H_2S concentration from 0.2 to 5 ppm at room temperature, and its CV shows a good reliability which is less than 5% to H_2S/1Au cases.

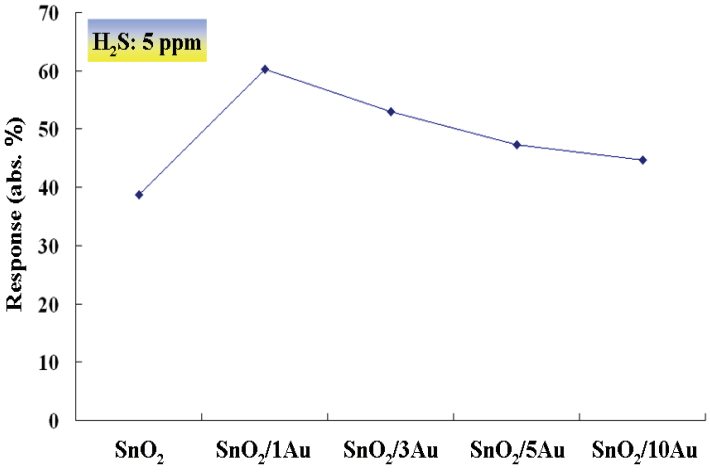

Figure 3: The doping effect of nano-gold particles in SnO2 sensing filr. (a)SnO_2, (b) SnO_2/1Au (c) SnO_2/5Au (d) SnO_2/10Au. (400□calicined temperature)

The electron transfer was due to the depletion formation when H2S molecules adsorbed on tin oxide which caused energy gap to enlarge and induce the film resistance increase. The formation of depletion region was produced from the aging process of tin oxide grain mainly. Therefore, when tested gas passed into the chamber, the tin oxide film will adsorb oxygen ions and release the electronics into conduction band. This mechanism will promote the increase of sensing film electron concentration and conductance. Its reaction equation is shown as equation (1).

$$H_2S + 3O_{2\,(ads)}^{-} \rightarrow H_2O_{(g)} + SO_{2\,(g)} + 6e^{-} \quad (1)$$

Moreover, for a gas sensor developing, the selectivity is very important. In this study, we used 5 ppm of SO_2, 50 ppm of NH_3 and 0.1% CO_2 gas to test the selectivity of self developing H_2S sensor. The results showed that the tin dioxide thin films with gold particles doping (SnO_2/1Au) had the best selectivity and anti-interfere ability. The SNR (signal to noise ratio) for SnO_2/1Au film was 2.4 and it was higher than other types of tin oxide composition.

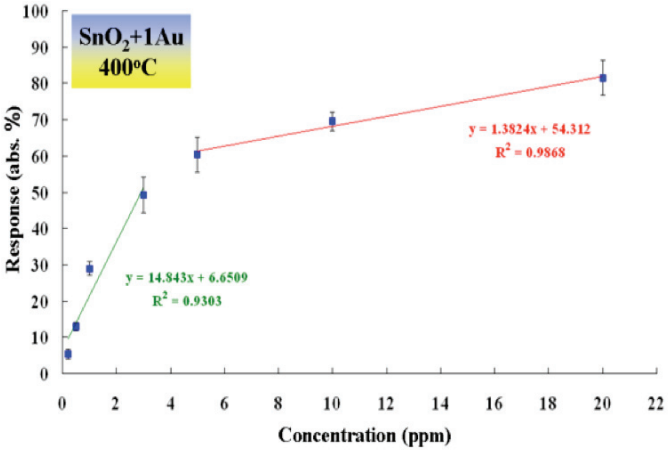

Figure 4: The calibration curve of SnO2/Au gas sensor.

3.3 Selectivity in SnO2/Au sensor

Fig. 5 shows the selectivity, the sensitivity for H2S gas is higher than those for other gases. Those for SO2, NH3, CO2 and O2 gas detection, the results shows these conductive responses were increase and the variation limited up to 10% maximum. We also calculate the signal to noise ratio (SNR) to SO2, NH3, CO2 and O2 for SnO2/1Au; the SNRs are 4.37, 10.5, 18.8 and 5.43, respectively. The film composition of SnO2/1Au had a maximum SNR than others; we referred this result to its grain particles. According to our SEM image, the particle size of film (composed by SnO2 +1 Au) is 50-100 nm. If we increased the composition of gold, the particle size presented a downward trend, the grain size down to 30-70 nm. In general, smaller grain particles also induce a bigger noise signal from interference gases.

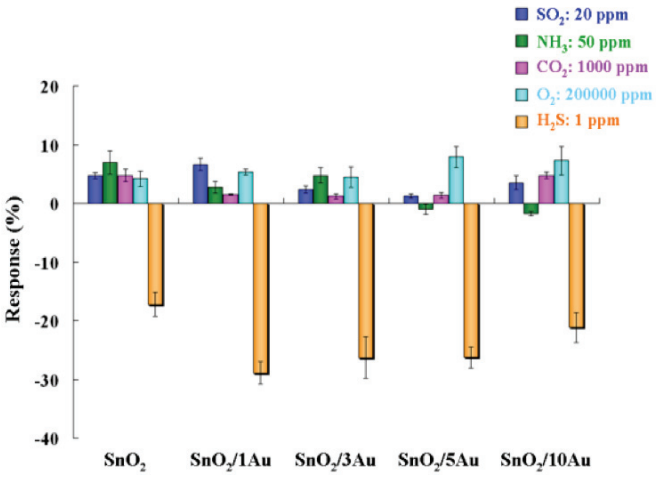

Figure 5: The selectivity of SnO2 sensing film

4 CONCLUSIONS

In this study, we successfully used the sol-gel method to make the tin oxide sensing film for hydrogen sulfide detection. Moreover, we improved the sensitivity and selectivity of tin oxide sensing film with the doping of different ratio gold nano-particles. The best composition for tin oxide and gold nano particles is SnO_2/1Au which can get the best sensitivity and selectivity. Moreover, the detection limit of this sensor can reach to 0.2 ppm at room temperature for daily environment monitoring.

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