Thin Film-Resistive Gas Sensor with SnO_2/Au Nanocomposite for Hydrogen Sulfide Detection

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ABSTRACT

A highly sensitive and selective H_2S gas sensor has been developed by deposited a SnO_2 thin film on an alumina substrate with a spin-coated method. This SnO_2 sensing film was be made by a sol-gel method, and for getting a good sensitivity and selectivity we doping a mixture composite by Au nanoparticles with SnO_2. In charactering of this sensing film, we used X-ray diffraction to analyze the composition of SnO_2/Au nanocomposites, and used the SEM and TEM images for observing the morphology and the particle size, the data shown the calcined temperature which set at 400 ℃ was the best calcinations temperature. The results of experiments showed that for hydrogen sulfide detection, there have a good linear response in SnO_2+1Au composites, the detection range was from 0.2 ppm to 0.5 ppm at room temperature, and the selectivity the sensor shown that in Au doping composites have a good selectivity to H_2S against SO_2, NH_3 CO_2 O_2 and alcohol. The sensor had speedy response kinetics to H_2S, the 90% response time to 0.2 ppm H_2S was 60 s, and the recovery time was 30 s. We also studied the effect of humidity (50%, 70% and 80% RH) to H_2S detection. The result showed the influence of humidity that was needed to be concerned in practical use.

Keywords: hydrogen sulfide, tin dioxide, gold nano-particle

1 INTRODUCTION

Hydrogen sulfide (H_2S) is a colorless gas that has strong odor of rotten eggs. H_2 S poisoning is a rarity, mainly observed in industrial settings. Emergency physicians must be aware of the presentation and management of H_2S poisoning because rapid identification and treatment is essential for recovery. If long-time exposure to 10 ppm H_2S environments, the health of peoples will cause some degree of damage [1], so it is necessary to prevent by the use of gas sensor, However, the H_2S sensor from market sales is not only expensive but also larger and operates at higher temperature, it is not suit for operating in room temperature and low concentration detection. In the past several decades, with tin oxide as base material of the semiconductor metal oxide materials are one of the most widely used gas sensing materials, Tin oxide material is simpler on sensing element fabrication, and it can overcome the problems of selectivity and operational temperature by doping some noble metals or metal oxides such as: palladium, platinum, silver, copper oxide, tungsten oxide, and iron oxide [2]. Existing methods for detection of H_2S gas are based on materials and apparatus at macroscopic scale [3-6]. These include the use of gas chromatography, laser spectroscopy, surface acoustic wave, tin oxide and gold thin films. In contrast to these traditional sensing methods, increasing interest has been directed to miniaturization and the development of a nano-scale H_2S sensor as a small sensing device offers clear advantages in many ways [7, 8]. For example, an array of sensing units may be constructed on a small chip by integration, and the sensor may be particularly suitable in an environment where the working space is very limited such as 'downhole' detection of H_2S gas in oil wells [9]. 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.

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 ($SnCl_4 \cdot 5H_2O$) 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.

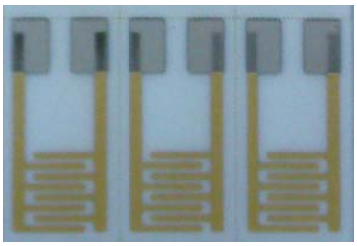

Fig. 1 the photography of SnO_2/Au film on interdigital electrode for H_2S detecting.

3 RESULTS AND DISCUSSION

3.1 Morphology study of SnO_2 film

Tin dioxide grain size and shape analyzed by TEM is shown in Fig. 2(a). Results show that when the calcination temperature at 300 ℃, the particles morphology seemed not to be obvious, if we increased the calcination temperature up to 400 ℃, the particles of tin dioxide formatted obviously. Therefore, we set 400 ℃ as the best calcination temperature. After then, we compared this result to SEM image, the result showed in Fig 2 (b). The particle size of film (composed by SnO_2 +1 Au) that had no significant difference to SnO_2, the average grain size of about 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, we referred this phenomena that could cause by the incorporation of gold stacked high difference to increase the nucleation sites.

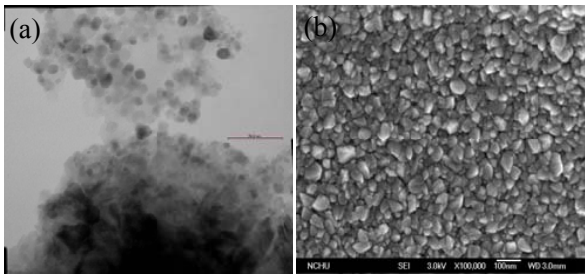

Fig. 2 images of SnO_2 sensing film. (a)SEM image, (b) TEM image.

3.2 XRD analysis of SnO_2 film

Fig. 3 shows the X-ray diffraction (XRD) analysis to tin oxide and tin oxide/gold powder on 400 ℃ calcined temperature. The crystalline of tin oxide formed mainly by 110, 101 and 211 phase, and their diffraction peak (2θ angle) were 27°, 34° and 51.9°, respectively. This result does consist with Liu H., Das S., and Wang GX [4-6]. No gold peak was formed in the crystal structure of tin dioxide, that's due to the lower gold content which cannot form a large grain size. We also used XRD method to confirm whether the presence of other impurities such as residual chloride or tin oxide formation. For SnO_2/1Au case, it characterized peak shows a smaller and narrow trend than SnO_2 case, the reason is referred to the effect of Au particles adding [7]. Au particles adding will decrease the

size of SnO_2 grain, and this phenomena also can be verify by Scherrer's formula in XRD spectrum, $D = 0.9\lambda/\beta\cos\theta$ (here D is the grain size, λ is the radiation wavelength, β is the wide of half peak, θ is the diffraction peak angle) [5], so when β is greater, grain size of D is smaller.

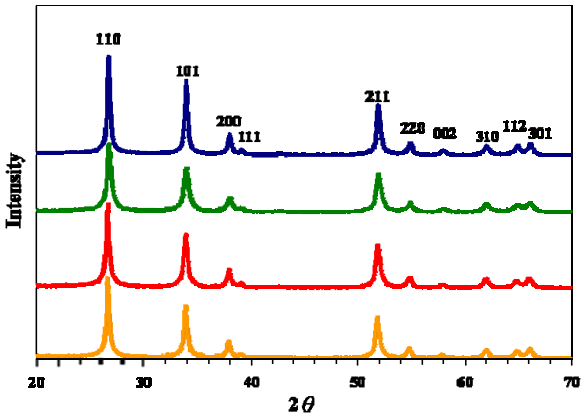

Fig. 3. X-ray diffraction spectrum, (a)SnO_2, (b)SnO_2/1Au, (c)SnO_2/5Au, (d)SnO_2/10Au in 400 ℃ calcined temperature.

3.3 Calcined temperature effect on sensitivity

The figure 4 shows the sensitivity test for 1ppm SnO2 in different calcined temperature. The 400 ℃ calcined temperature showed the best sensitivity for H_2S detection. When the temperature low than 400 ℃, The SnO_2 showed an amorphous phase structure, so the sensitivity was lower than crystal structure. When the calcination temperature higher than 400 ℃, the grain size increased, it to make the sensitivity of hydrogen sulfide sensor decrease.

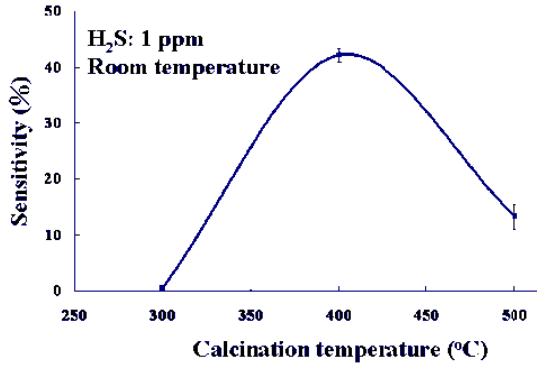

Fig. 4. The sensitivity test of SnO_2 to different calcined temperatures on 1 ppm H_2S.

3.4 Calibration curve of H_2S sensor

Figure 5 is 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.

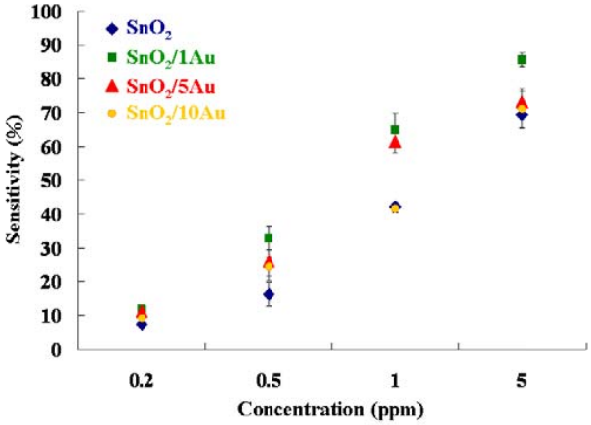

Fig. 5. The calibration curve for H2S detection at 400℃ calicined temperature. (a)SnO_2, (b) SnO_2/1Au (c) SnO_2/5Au (d) SnO_2/10Au.

The electron transfer was due to the depletion formation when H_2S 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 [9]. 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).

$$H_2S + 3O_2^-{}_{(ads)} \; H_2O_{(g)} + SO_{2\,(g)} + 6\,e^- \qquad (1)$$

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.

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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