SnO$_2$ microrods based triethylamine gas sensor

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Abstract. Triethylamine (TEA) gas sensor having high response and stability are in great demand in the actual working environment. In this paper, SnO$_2$ microrods are prepared on SiO$_2$ (300 nm)/Si substrate by thermal evaporation. The SnO$_2$ microrods-based gas sensor is successfully prepared. The gas response and stability of the sensor are tested at an optimal temperature of 200 °C. When the sensor is exposed to 100 ppm TEA gas, the response time is only 4 s. The detection limit is below 1 ppm. The gas-sensing mechanism is further discussed.

1. Introduction

In the past few decades, the rapid development of science and technology has promoted the continuous advancement of society, and the living standards of people have been greatly improved. At the same time, it also brings many negative impacts to the whole society, such as increased emissions of harmful gases and pollutants, which poses a serious threat to public health. Therefore, it is imperative to monitor and detect toxic, harmful, flammable and explosive gases in working and living places [1-3]. Among the harmful gases, TEA gas is the most widely concerned. It is often used in the industrial field and is a volatile organic compound with irritating odor, toxic, flammable and explosive, which can cause lung problems, skin burns, and even death. TEA gas can be secreted from dead fish, marine organisms and seashells. Therefore, it poses a huge threat to marine life, water resources, and multiple biological chains. According to the Occupational Safety and Health Administration, the concentration of TEA in the air should not exceed 10 ppm [4-6].

Metal oxide semiconductor (MOS) are widely used because of their reliable sensitivity, low cost, high stability, and long life. Among many kinds of MOSs, SnO$_2$ is the most widely used, and it has a wide band gap (E$_g$ = 3.6 eV, T = 300 K), high electron mobility, good chemical, and physical stability, etc [7, 8]. One-dimensional (1D) SnO$_2$ nanomaterials have a large relative specific surface area, the gas sensors based on 1D SnO$_2$ nanomaterials have excellent gas sensitivity performance [9]. Holguin-Momaca J. T et al. [10] successfully prepared SnO$_2$ nanowires by vapor-liquid-solid method, but a mixture of Ar, O$_2$, and H$_2$ was required during the preparation. It is well known that the mixture of O$_2$ and H$_2$ will explode under certain conditions, so the experimental process is dangerous. A. Kolmakov et al. [11] reported that the gas sensing reaction of SnO$_2$ nanowires and nanobelts under the action of Pd catalyst is good, but the preparation process is complicated and not effective for detecting TEA gas.
Therefore, it is extremely urgent to develop a 1D SnO$_2$ gas sensor with the simple preparation process, high sensitivity, good stability, and reliability.

In this paper, Sn and SnO mixed powder were used as the source material, and the uniform SnO$_2$ microrods were successfully prepared by a simple thermal evaporation method. This method is not only easy to operate, but also repeatable and reliable. The SnO$_2$ microrods sensor has a fast response to TEA, good stability, and low detection limit.

2. Experimental

2.1. Preparation of SnO$_2$ microrods

We successfully prepared a large number of uniform SnO$_2$ microrods on SiO$_2$ (300 nm)/Si substrates by thermal evaporation. Firstly, Sn and SnO mixed powder with a mass ratio of 5:1 were placed at one end of the quartz plate, and several substrates positioned at the other end (about 1 cm apart), which had sputtered with an Au film of about 3-4 nm. Second, the quartz plate is placed in the center of the quartz (the powder is upstream of the gas flow), and the thermal tube is closed, and then vacuumed. After the gas pressure in the furnace is stabilized to 100 Pa, Ar gas (60 sccm) is introduced. Then, it is automatically carried out according to the set program (up to 1000 °C at 10 °C/min, and kept for 60 min). Finally, the samples were taken out after cooling naturally to room temperature. A large number of white wires were found on the substrate surface and were characterized by XRD, Raman, and SEM. Au acts as a catalyst during growth, so the growth mechanism can be ascribed to vapor-liquid-solid growth mechanism [12, 13]. The growing process is shown in Fig. 1.

![Figure 1](image-url)

**Figure 1.** (a) Schematic diagram of the growth process of SnO$_2$ microrods; (b) Schematic diagram of the growth of SnO$_2$ microrods on SiO$_2$/Si substrate.

2.2. Gas sensing test

The sample was sputtered Au film electrodes (7 mm × 3 mm × 0.1 mm) on the surface. Then, the gas sensor was dried in a vacuum at 100 °C and aged for 24 h to give it better stability and repeatability. The gas-sensing performance was tested using a commercial gas sensing analysis system. The test sensor was placed in a ventilated 18 L sealed chamber. Gas sensitivity experiments (using micro-injectors) were carried out at various temperatures ranging from room temperature to 300 °C for obtaining an optimum temperature. Using the following formula to define the gas sensing response:

\[
S = \frac{R_a}{R_g}
\]
$R_a$ is the resistance of the test sensor in air, and $R_g$ is the resistance of the test sensor in the target gas. The response and recovery time was calculated as reached a 90% variation in resistance of the difference from the maximum after injecting target gas and backing to air [14].

3. Results and discussion

3.1. Characterization

In order to study the sample structure, we performed XRD structural characterization. As shown in Fig. 2(a), the plurality of diffraction peaks were observed. The Au (111) crystal plane was observed at 20 = 38.50° (Au derived from the catalyst). There are three strong diffraction peaks at 20 = 26.84°, 34.16°, and 52.04°, corresponding to the SnO$_2$ (110), (101), and (211) crystal planes respectively, which is consistent with the rutile structure SnO$_2$ standard card (JCPDS 41-1445). No other peaks were detected in the XRD pattern, indicating that the Sn and SnO mixed powder were completely converted to SnO$_2$, and the purity of the sample is high. The XRD diffraction peaks of the sample are sharp and the half-height width is narrow, indicating that the prepared SnO$_2$ samples had high crystallinity [15]. To further investigate the sample structure, we also performed Raman test. Fig. 2(b) shows the room temperature Raman spectra of SnO$_2$ microrods. The Raman scattering peaks correspond to the E$_g$, A$_{1g}$, and B$_{2g}$ vibration modes of the rutile structure SnO$_2$ at 474.85 cm$^{-1}$, 633.29 cm$^{-1}$, and 773.5 cm$^{-1}$. It is further confirmed that the prepared SnO$_2$ microrods have the rutile structure, which agrees with the XRD results presented.

![Figure 2](image_url)

**Figure 2.** (a) XRD pattern of SnO$_2$ microrods; (b) Raman scattering spectra of SnO$_2$ microrods

The morphology of SnO$_2$ microrods was characterized by scanning electron microscope (SEM). As shown in Fig. 3(a), it shows that a large number of rods-like are coated on the surface, and the prepared microrods are uniform and the length is up to 10 μm. In Fig. 3(b), the diameter of the microrods is about 600 nm, the ratio of the length to diameter is up to 16. The microrods surface is rough and some white points are coated on the whole surface.
3.2. Gas sensing performance

The operating temperature of the gas sensor is one of the important factors to evaluate the quality of the device. In order to explore the optimal temperature of gas sensor, we conducted tests to 100 ppm TEA gas at different temperatures (100, 150, 200, 250, and 300 °C), and obtained responses of 1.28, 1.7, 2.6, 1.8, and 1.5 at 100, 150, 200, 250, and 300 °C, respectively. At 200 °C, the sensor got the highest gas response. Thus, the optimum operating temperature can be recognized as 200 °C, which is shown in Fig. 4(a). The following systematically tested gas sensing is all at 200 °C. In Fig. 4(b), it was found that the gas response increased with the increasing concentration ranging from 1 ppm to 500 ppm. When the concentration is 1 ppm, the gas response is 1.6, and when the concentration is 500 ppm, the gas response is up to 4. This gas sensor not only has a good gas-sensitive response to TEA gas but also has a low response limit (less than 1 ppm). We also analyzed the response/recovery property as exposure to the TEA gas concentration of 100 ppm. In Fig. 4(c), the gas sensor has a fast response time (4 s) and a fast recovery time (20 s). Stability is also one of the important factors in describing sensors’ performance. We tested the stability of the gas sensor, which is shown in Fig. 4(d). The sensor was tested with 13 cycling times within 2000 s at a TEA gas concentration of 100 ppm, and the cycling response shows no obvious change, indicating that the sensor has good stability.

Based on the above results, the gas mechanism is discussed. Generally, when the TEA gas sensor was exposed to the air, the oxygen molecules in the air would be adsorbed on the surface of the SnO$_2$ microrods, and are ionized to formed O$^\delta$(O$_2$-, O$^-$, and O$^2$-) by capturing free electrons from the conduction band of SnO$_2$. Thus, an electron depletion layer is formed by reducing the free electron concentration, and the energy band of the SnO$_2$ microrods is bent upward, the resistance would increase. The detail is shown in Fig. 5(a). When the sensor was exposed to TEA gas, as shown in Fig. 5(b), the TEA gas would react with O$^\delta$ adsorbed on the surface of the SnO$_2$ microrods. The reactions can be calculated by the following equation:

$$(\text{C}_2\text{H}_5)_3\text{N} + O^\delta \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{CO}_2 + e^-$$ (2)
Figure 4. (a) The gas response to 100 ppm TEA gas at different temperatures (100-300 °C); (b) The gas response under different TEA gas concentrations; (c) The response time of the gas sensor; (d) The stability of the gas sensor.

The released electrons would return to the SnO$_2$ conduction band, and narrow the energy band bending, the electron depletion layer would be thin, and the resistance reduced accordingly [16, 17], the gas response obtained.

Figure 5. Schematic of the SnO$_2$ microrods gas sensing mechanism. (a) The oxygen is adsorbed on the surface of the SnO$_2$ microrods and the depletion layer formed; (b) the depletion layer shown under TEA gas; (b) Energy band diagram of the Au/SnO$_2$

There is another effective factor to contribute to resistance reduction. The XRD pattern revealed that there were Au diffraction peaks, indicating that Au was doped into the SnO$_2$ microrods, they would form Au/SnO$_2$ heterojunctions. As shown in Fig. 5c, For the Au/SnO$_2$ heterojunctions, because of the different work function between Au (5.1 eV) and SnO$_2$ (4.5 eV), after contacting, the electron would transfer from SnO$_2$ to Au and decrease the resistance. In addition, the existence of Au augments the n-type
property of SnO$_2$ due to the metal-semiconductor junction. Au induces a great charge depletion, TEA gas molecules are attracted. The adsorbed TEA gas molecules react with the absorbed oxygen ions, and then the captured electrons are released, leading to the thickness of the depletion layer decrease and the resistance are decreased, which is contributing to enhance the gas-sensing performance [18-20].

4. Conclusion
In summary, we prepared uniform SnO$_2$ microrods by simple thermal evaporation. The structure property and morphology of SnO$_2$ microrods are confirmed by XRD, Raman, and SEM characterization. The SnO$_2$ microrods-based gas sensors showed the great advantages of fast response, high stability and low detection limit to TEA gas. The gas-sensitive mechanism is also discussed. This work provides a simple and reliable method for preparing SnO$_2$ microrods-based TEA gas.

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