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UV-activated room temperature metal oxide based gas sensor attached with reflector

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ABSTRACT

A UV light enhanced gas sensor with light reflector was designed and fabricated. Compared with that without reflector, the sensor with reflector had higher efficiency of UV light absorption and utilization. The sensor with reflector exhibited higher response to ethanol than that without reflector at room temperature. The response of the sensor with reflector to 100 ppm ethanol was about 160 under UV illumination. Moreover, the response and recovery kinetics were obviously improved, and the response and recovery time were 50 s and 150 s, respectively. Such obvious improvement on the sensing performance for the sensor can be ascribed to the increasing of the optical path length in the sensing material layer, due to the introduction of the reflector.

1. Introduction

Semiconducting oxide gas sensors have drawn many interests for their obvious advantages, e.g., high sensitivity, small size and low cost. In order to obtain the excellent sensing performance, the sensors are usually operated at high temperatures of 100–400 °C. However, such high temperature not only can lead to high power consumption but also ignite the flammable and explosive gases. Moreover, the long-term application at high temperature could result in the growth of the oxide grain that is a main factor responsible for the long-term drift problem. In the recent years, some strategies, such as doping [1–3], MEMS fabrication [4], nano-sensing materials [5] and UV (ultra-violet) illumination [6–10] have been used for reducing operating temperature. Among them, UV illumination is a promising alternative. Since Camagni et al. first reported the UV enhanced semiconducting oxide sensor in 1996 [11], many reports have shown that UV illumination could obviously improve the sensing performances of semiconducting oxide gas sensors [12–14]. However, most of the researchers focus on the design and preparation of the new sensing materials. The study about the effect of the sensor structure on the sensing performance was rarely reported. Up to now, the reported UV illumination gas sensors usually utilize the tubular structure, while the planar structures have been rarely proposed [15,16,19]. Compared with the tubular structure, the planar sensor has higher utilization of UV light. But, for the reported planar type sensor, due to the adsorption and the transmission of substrate, the utilization of UV light is greatly decreased. Although the illumination effect on the sensing performance could be enhanced by increasing the light intensity [11,17], the big and expensive light source is demanded. Thus, it is unsuitable for constructing a compact and low-cost gas sensor.

In this work, a small commercial light-emitting dioxide (LED), which has weak light intensity, was used as the light source. So, increasing the UV utilization becomes very important for the sensor. In order to increase the utilizing efficiency of the UV light, we proposed a planar type gas sensor with light reflector. The gas sensing performance of the planar type sensors with and without light reflector was investigated.

2. Experimental

2.1. Fabrication of sensors

In our previous work [18], it has been examined that the hollow sphere (HS) SnO_2–TiO_2 showed a good response to ethanol under UV illumination. Therefore, in this work, HS SnO_2–TiO_2 was used as sensing material. A Pt interdigitated electrode was formed on the quartz substrate with screen printing technique, and the electrode gap was about 100 μm. An Al light reflector with the thickness of about 400 nm was deposited on the backside of the quartz substrate using thermal evaporation method under vacuum condition (5×10^{-6} Pa). The sensing layer of the planar sensor was formed as follows: first, 10 mg HS SnO_2–TiO_2 powder material was added into ethanol and dispersed under ultrasonic condition

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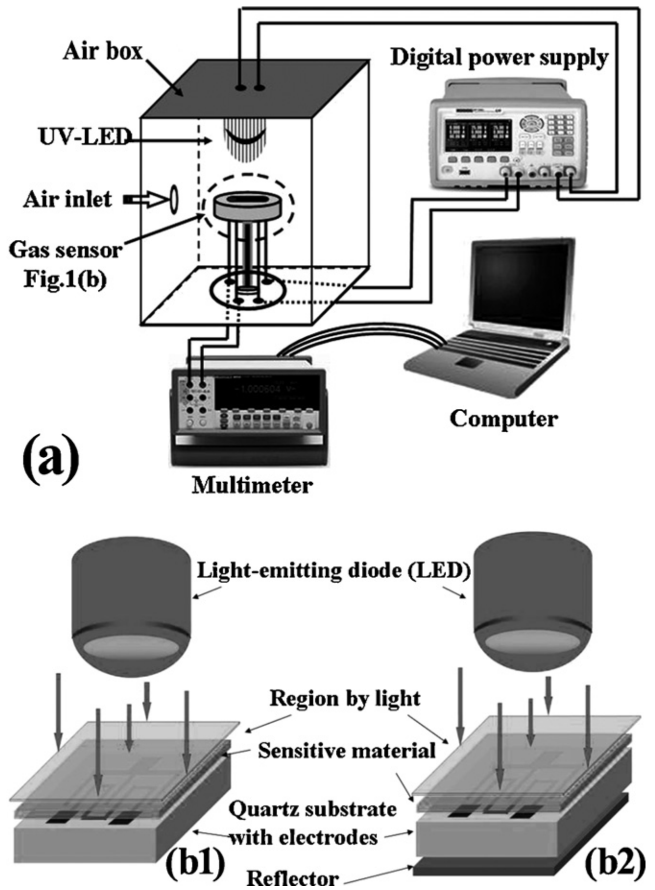

Fig. 1. Testing system for gas sensing properties (a) and structure diagrams of two kinds of sensors (b), (b1) is planar type sensor without reflector and (b2) is planar type sensor with reflector.

for 5 min to obtain a uniform suspension; second, the quartz substrate (2.4 mm × 2.5 mm) was horizontally put into a square container with the bottom area of 17.3 mm × 17.3 mm; then the as-prepared suspension was poured into the container and kept at room temperature until ethanol completely evaporated, thus 0.2 mg HS SnO_2–TiO_2 was deposited on the quartz substrate; finally, the formed sensing layer was sintered at 500 °C for 2 h. For obtaining the different thickness of sensing layer, the same operating process was repeated.

2.2. Characterization of morphology and thickness

The morphologies of sensing layers were observed by field-emission scanning electron microscopy (JEOL JSM-7500F), operated at an acceleration voltage of 15 kV. The thicknesses of sensing layer were measured by stylus profilers (KLA-Tencor, D100, U.S.A.). The weight was measured by analytical balance (Mettler Toledo, AB135-S, Switzerland).

2.3. Measurement of gas sensing properties

As above described, a UV-LED (peak wavelength 380 nm; operating voltage 3 V) was utilized as the light source of the UV illuminated sensor. Schematic diagrams of the testing system and the structures of the planar sensors with and without reflector are displayed in Fig. 1. The UV-LED illuminated the sensing material from upside direction. The distance between the UV-LED and the gas sensor was 2 mm. The power of the UV-LED at this distance was 0.7 Cd/m^2 (measured by PR650, California, U.S.A.). Before measuring, the sensor was first irradiated with UV-LED for 30 min for obtaining the stable sensing properties. The temperature (20 °C) and humidity (10% RH) of the test chamber were well controlled with a humidity/temperature controlling chamber (Espec SETH-EZ-020R, China) during the measurement. The desired ethanol concentration was obtained by evaporating the certain volume of liquid ethanol in the testing chamber. For the other gases like CO, NH_3 and H_2S, the desired concentration was gained by mixing a known volume of standard gas (1000 ppm) with air. The resistances of the sensor in air and target gas were measured with a digital precision multimeter (Fluke, 8846A, U.S.A.) which was connected to personal computer (PC) for data processing. The response was defined as Ra/Rg. Here, Ra and Rg are the resistances of the sensor in air and target gas, respectively.

3. Results and discussions

The SnO_2–TiO_2 hollow spheres were uniformly deposited on the substrate and the continuity of the film were gradually improved with increasing the thickness of sensing layer. The SEM images of sensing layers with 1, 5 and 10 deposited layers were shown in Fig. 2 (a), (b) and (c), respectively. When the times of the deposition were less than 5, the sensing layer was not continuous (Fig. 2(a)) and could not be applied for fabricating a sensor. But, with the increasing of the deposition times, the sensing layer became continuous and has loose and porous morphology, as shown in Fig. 2(b) and (c). Such morphology was benefit for gas absorption and light incidence into the inner of the sensing layer.

The correlation between the thicknesses of sensing layer and the deposition times is shown in Fig. 3. It is obvious that the thickness linearly increases with the deposition times. An average thickness for each deposition was about 2.2 μm. Thus, when the times were 10, the thickness of the sensing layer was about 22 μm.

The relationship of the response to 100 ppm ethanol and the thickness of sensing layers for the sensors with and without reflector are shown in Fig. 4. For the sensor without reflector, when the thickness of the sensing layer was thinner than 26.5 μm, the response increased with the thickness of the sensing layer, because a larger number of active sites would be supplied on the surface of the sensing material, meanwhile, the dense contacts were formed among SnO_2–TiO_2 hollow spheres, which was beneficial to the transfer of the electrons [22]. When the thickness was larger than 26.5 μm (about 12 layers), the response to 100 ppm ethanol became constant. This is because that although the amount of the active sites increases with increasing the thickness of the sensing layer, the ethanol molecules could not reach the deep inner of the sensing layer which cannot contribute to the response.

For the sensor attached with reflector, the response first increased with the thickness of the sensing layer, up to 22 μm (10 layers) and then gradually decreased. The obtained maximum response to 100 ppm ethanol was about 160 at 22 μm. The response of the sensor with reflector to 100 ppm ethanol was larger than that of without reflector at the same thickness. However, when the thickness reached 33 μm, the response of the sensor with reflector was almost same as that of the sensor without reflector. Such phenomenon can be ascribed to that the intensity of the reflecting light becomes weak with increasing the thickness of the sensing layer. When the thickness of sensing layer varied from 11 to 22 μm, although the intensity of the reflecting light was decreased, the reflecting light still could completely penetrate through the sensing layer and activate all sensing layer once again. Moreover, because thicker sensing layer contained more sensing materials which provided a larger number of active sites, the response would be raised with increasing the thickness. At 22 μm, the reflecting light can just pass through the sensing layer and be most effectively utilized, so