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Enhancement of H_2 Sensing Properties of In_2O_3-based Gas Sensor by Chemical Modification with SiO_2

Zi Li ZHAN[1]*, Deng Gao JIANG[1], Jia Qiang XU[2]

[1]School of Chemical Engineering, Zhengzhou University, Zhengzhou 450002
[2] Department of Chemical Engineering, Zhengzhou Institute of Light Industry, Zhengzhou 450002

Abstract: The sensitivity and selectivity to H_2 of a new In_2O_3-based gas sensor were improved significantly by surface chemical modification. A dense layer of SiO_2 near the surface of the porous In_2O_3 bead was formed by chemical vapor deposition (CVD) of diethoxydimethysilane (DEMS). The dense layer functioned as a molecular sieve, thereby the diffusion of gases with large molecular diameters, except for H_2, was effectively controlled, resulting in a prominent selectivity and high sensitivity for H_2. The working mechanism of the sensor was also presented.

Keywords: H_2 gas sensor, indium oxide, molecular sieve.

Improvement of sensitivity and selectivity of *n*-type metal oxide gas sensors is one of the most important subjects to meet increasing demands for more intelligent gas sensing. Use of a catalyst layer [1] or a gas filter layer[2–4] on the sensor surfaces is an approach for improving the gas selectivity of the sensor.

Indium oxide is a new important material for a semiconductor gas sensor. In_2O_3-based gas sensors exhibited some excellent gas-sensing properties[5]. In our previous paper, we reported In_2O_3-based LPG[6] and combustive gas sensor[7]. In present work, the target was to improve the selectivity of In_2O_3-based gas sensor.

Experimental

The nanometer-sized In_2O_3 prepared by a reverse microemulsion method[8], and the gas sensor was fabricated based on hot wire type gas sensor[7].

In order to improve the properties of the above element, the surface-modifying process was employed. A dense layer of SiO_2 was formed near the surface of the porous bead by the CVD of DEMS. The gas sensors were placed in one term of a quartz tube, which was placed in a tube-type electric furnace. Then the saturated vapor of DEMS was injected in the quartz tube heated at 600℃ for 20 min. DEMS was decomposed thermally to silica and deposited in the pores, presenting in the surface layer of the gas sensor, resulting in a dense layer that worked as a molecular sieve, which allowed selective diffusion of hydrogen through the pores present in the surface layer of the gas sensor.

* E-mail: Zhanzili@zzu.edu.cn

Gas sensitivity (△V) is defined by the difference between the sensor output in a sample gas balanced with air (Vg) and in a clear air (Va): ΔV=Vg-Va.

In clear air, the sensor output (Va) was adjusted to zero by adjusting the resistance potentiometer, so the sensitivity: △V=Vg.

Result and Discussion

Figure 1 and **Figure 2** show the cross sensitivity of the sensor to H_2, CH_4, *i*-C_4H_{10} and C_2H_5OH unmodified and modified with SiO_2, respectively. The sensitivity to 0.1%H_2, CH_4, *i*-C_4H_{10} and C_2H_5OH of the unmodified gas sensor was 167, 117, 137, 70 mV, respectively, but that of modified sensor was 593, 20, 82 and 182 mV, respectively. Compared **Figure 1** with **Figure 2**, a prominent selectivity and high sensitivity of the modified gas sensor to H_2 were obtained. The improvement of selectivity and sensitivity to H_2 is probably due to the molecular size effect.

Figure 1 The cross sensitivity of the sensor unmodified with SiO_2

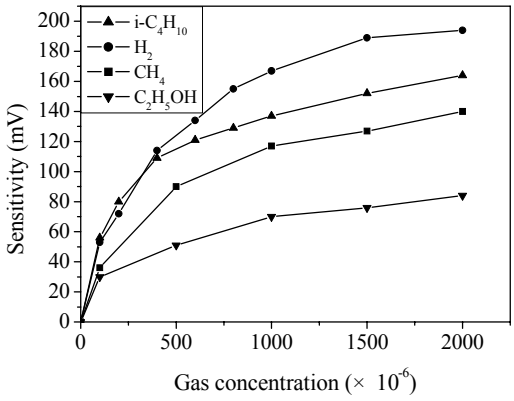


Figure 2 The cross sensitivity of the sensor modified with SiO_2

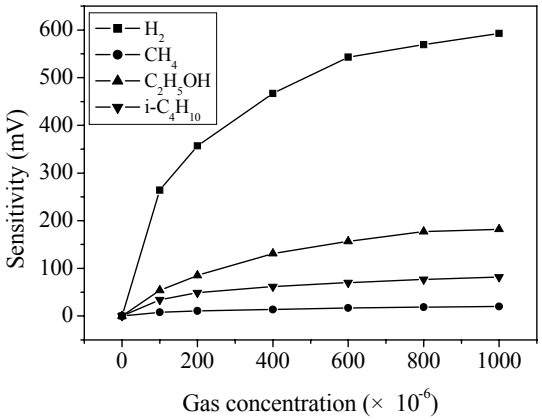


Figure 3 A simple model for selectivity and sensing mechanism to hydrogen in the indium oxide layer with a dense surface layer(molecular sieve).

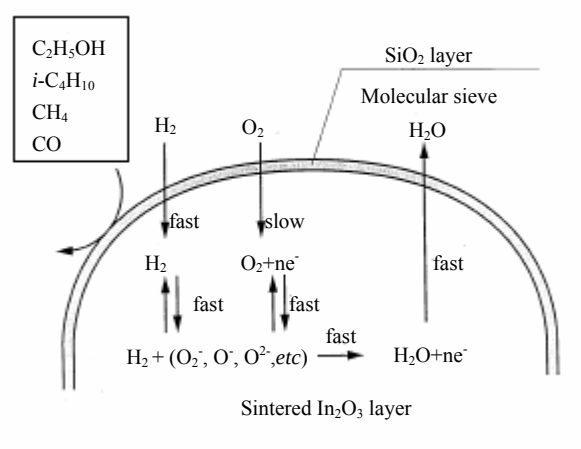


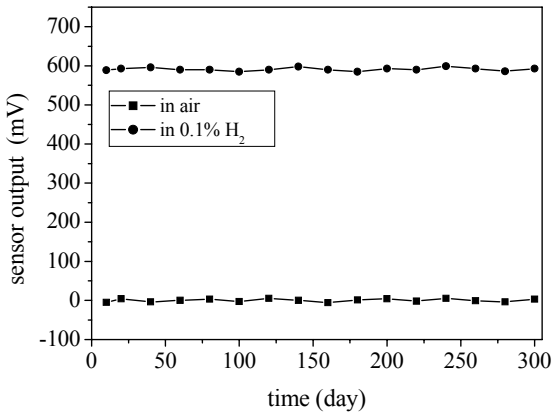
Figure 3 shows the probable sensing mechanism. The conductivity of the indium oxide is governed by a steady concentration of the adsorbed oxygen ions determined by chemical dynamics including oxidation and diffusion, as shown in **Figure 3**. In addition, the molecular diameters obtained from viscosity of gases H_2, H_2O, O_2, CH_4, and i-C_4H_{10} are 0.218, 0.272, 0.296, 0.380, and 0.5 nm, respectively [9].

Hydrogen with the smallest molecular diameter can easily penetrate through the surface dense layer. It is activated on the surface of indium oxide and reacts very quickly with adsorbed oxygen species (O_2^-,O^-,O^{2-}, *etc.*) with negative charges, resulting in water and free electrons. As a result, the conductivity of the indium oxide semiconductor increases. Oxygen with the larger molecular diameter is diffusion-controlled by the surface dense layer, both the oxygen gas concentration in the pores and the surface density of the adsorbed oxygen species are apt to decrease significantly, while the reaction of oxygen with hydrogen is fast. The water produced *via* the oxidation of hydrogen in the inner layer is supposed to pass through the dense layer and release easily out of the inner layer, because the water molecule has a somewhat small molecular size and is under vigorous thermal movement. The other reducing gases with molecular diameters larger than hydrogen are almost unable to invade and contact with the indium oxide owing to effective diffusion control by the surface dense layer. So hydrogen is most favorable for interaction with the indium oxide in the reaction system as shown in **Figure 3**.

The SiO_2 outer layer is also found to reduce permeation oxygen into the inner sensing layer (reaction zone) and the suppressed oxygen readsorption enhanced the gas sensitivity to H_2 [10].

Figure 4 shows the long-term stability of the gas sensor. The hydrogen selective gas sensor had a prominent long-term stability in atmosphere for about 300 days. The long-term drift of the sensor is less than 10 mV both in air and 0.1%H_2.

Figure 4 The long-term stability of the gas sensor



In a summary, a selective H_2 gas sensor, with a high sensitivity and prominent long-term stability was fabricated. The selectivity and sensitivity to H_2 of a hot wire type gas sensor were considerably increased by the surface modification with SiO_2, the layer of SiO_2 functioned as a molecular sieve, which allows selective diffusion of gas, resulted in a prominent selectivity and high sensitivity to H_2.

Acknowledgments

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