Gas sensors for oxides synthesis by hydrothermal and microwave hydrothermal methods

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Abstract: so far, gas sensors are playing an increasingly important role in environmental detection, agricultural production, medical treatment and other fields. Semiconductor oxide gas sensors are often used to detect toxic gases because of their low cost, simple manufacture, fast response, good selectivity and high sensitivity. There are many methods to prepare semiconductor oxides, such as hydrothermal synthesis, microwave hydrothermal synthesis and sol-gel synthesis. The advantages of hydrothermal synthesis and microwave hydrothermal synthesis are high economic efficiency and simple operation. The synthesized oxides have many different morphologies, such as zero dimensional, one-dimensional, two-dimensional, three-dimensional and so on. These different morphologies are conducive to gas diffusion and enhance gas sensing performance. Especially the hierarchical structure can greatly improve the gas sensing performance due to its large specific surface area, large porosity and high carrier concentration. This paper describes the SMO gas sensor prepared by hydrothermal method and microwave hydrothermal method.

Key words: gas sensor; Hydrothermal method; Microwave hydrothermal method

Introduction

In recent years, with the increasing improvement of people's lives and the rapid development of science and technology, more and more toxic and harmful gases are increasing. These toxic and harmful gases not only threaten people's lives and health, but also threaten people's property safety. Therefore, the detection of these toxic and harmful gases has become an urgent problem.

For the detection of these toxic and harmful gases, the most commonly used way is the detection of gas sensors. Among them, semiconductor metal oxide (SMO) gas sensor has a very important position. The reason why SMO gas sensor is important is that it has a series of advantages such as low cost, simple preparation, fast response, good selectivity and high sensitivity, which makes it stand out among many types of gas sensors.

Semiconductor metal oxide (SMO) can be divided into n-type SMO and p-type SMO according to most carrier types, and can also be divided into 0-dimensional, 1-dimensional, 2-dimensional and 3-dimensional SMO according to their morphology and structure. Generally, when the grain size of SMO reaches the range of 1-100 nm, the size of the material will be negatively correlated with the ratio of surface atoms to non surface atoms. The smaller the grain size of SMO is, the larger the ratio of surface atoms to non surface atoms is, which leads to unique chemical and physical properties.

There are many synthesis methods of oxide (SMO) for making gas sensors, such as hydrothermal synthesis method, solvothermal method, microwave hydrothermal synthesis method, electrospinning method, sol-gel synthesis method... Hydrothermal method has the advantages of low cost, simple operation and so on, which is more popular than other methods. The specific process of hydrothermal method is that the precursor is dissolved in water. Then, the above solution is heated to high temperature and high pressure in a closed container.

After a long time, the solution reaches the supersaturation state through the temperature difference, resulting in crystallization. Under normal circumstances, the chemical reaction will take 6 to 48 hours to nucleate and grow nanoparticles. Hydrothermal method is a slow heating process. The heat transfer mode of hydrothermal method is to transfer the heat to the reactor wall first, and then to the solution center. Its disadvantages are: (1) low efficiency; (2) Part of the heat energy is wasted; (3) Uneven heating.

The heating method of microwave hydrothermal synthesis is different from that of hydrothermal synthesis. The heating method of microwave hydrothermal method is to directly radiate the whole container. There are two mechanisms of microwave heating: (1) dipole rotation; (2) Ion conduction. The principle of dipole rotation is that polar molecules in the solvent heat the whole solution through the interaction of dipole rotation and microwave. The principle of ion conduction is based on the influence of microwave driving force on the types of ions in the solution. The solution is rapidly heated by Joule heating. Compared with hydrothermal method, microwave hydrothermal method has two advantages: (1) uniform heating; (2) Rapid synthesis. Microwave hydrothermal method belongs to the improvement of semiconductor material synthesis process. It can improve the reaction rate, perfect the parameter control, improve the repeatability, improve the yield, optimize the selective heating (reaction products in different mixtures in different microwave ovens), and realize automation. This means that the microwave hydrothermal method has the advantages of high production efficiency, convenient operation, wide application range and strong practicability. This paper aims to study the different morphology of SMO materials prepared by hydrothermal method and microwave hydrothermal method, and select the sensor with good gas sensing performance and low power consumption for analysis.

1 gas sensing mechanism

At present, SMO gas sensor has been widely used in the market with its unique advantages. It is of great significance to improve its sensing performance. The basic working principle of SMO gas sensor is to detect the target gas through the change of resistance. Researchers generally agree that the control theory of surface adsorbed oxygen is the gas sensing mechanism of SMO gas sensor.

The mechanism is mainly expressed as the change of the carrier concentration of SMO caused by the adsorption of oxygen molecules in the air on the surface of SMO. Due to different working temperatures, oxygen adsorbed on the conductor surface will capture electrons in the conductor and form oxygen anions (O2-, O-, O2-). When oxygen is ionized by electrons, oxygen anions adsorbed on the conductor surface form a space charge layer, which will cause the band bending inside the conductor, and the bending length is approximately equal to the thickness of the space charge layer.

According to the different types of SMO, the formation of space charge layers is different, which leads to different phenomena in the desorption process. The space charge layer formed by n-type SMO is electron depletion layer (EDL), and the space charge layer formed by p-type SMO is hole accumulation layer (HAL). The desorption process is the process of releasing the electrons captured by the oxygen anion back to the interior of the conductor. Zhao et al. Explained that when the n-type SMO sensor is placed in oxygen, oxygen is ionized into oxygen anions to form a very thick electron depletion layer (EDL) on the semiconductor surface, resulting in an increase in the resistance of the sensor. After the sensor contacts the n-butanol gas to be measured, the n-butanol gas molecule will react with the oxygen ions adsorbed on the surface of the material, and then the released electrons will return to the semiconductor, causing the carrier concentration to change, reducing the width of the space charge layer and the resistance of the sensor.

The resistance of p-type SMO increases in reducing gas. This is because the hole accumulation layer (HAL) is formed near the surface of p-type SMO due to free oxygen in the air. Secondly, when there is a chemical reaction between Hal on the surface of SMO and gas molecules, the free electrons will be put back into the p-type SMO, which greatly reduces the hole concentration and leads to the increase of resistance. Eun Kyung Suha also showed that when NiO based sensor reacts with hydrogen cation and oxygen ion in H2, the remaining electrons will reduce the number of holes, resulting in the rise of resistance.

From the perspective of gas sensing, the popularity of p-type SMO is far less than that of n-type SMO. As shown in Figure 1, the resistance of the core of n-type SMO is low resistance (Rcore), while the resistance of the electron depletion layer (EDL) on the SMO surface is high resistance (Rshell). The total resistance of the n-type SMO can be equivalent to the total resistance of the series connection between Rcore and Rshell. On the contrary, the core of p-type SMO has a high resistance (Rcore) and the hole accumulation layer (HAL) on the surface has a low resistance (Rshell). The total resistance of p-type SMO can be equivalent to the total resistance between Rshell and Rcore in parallel.

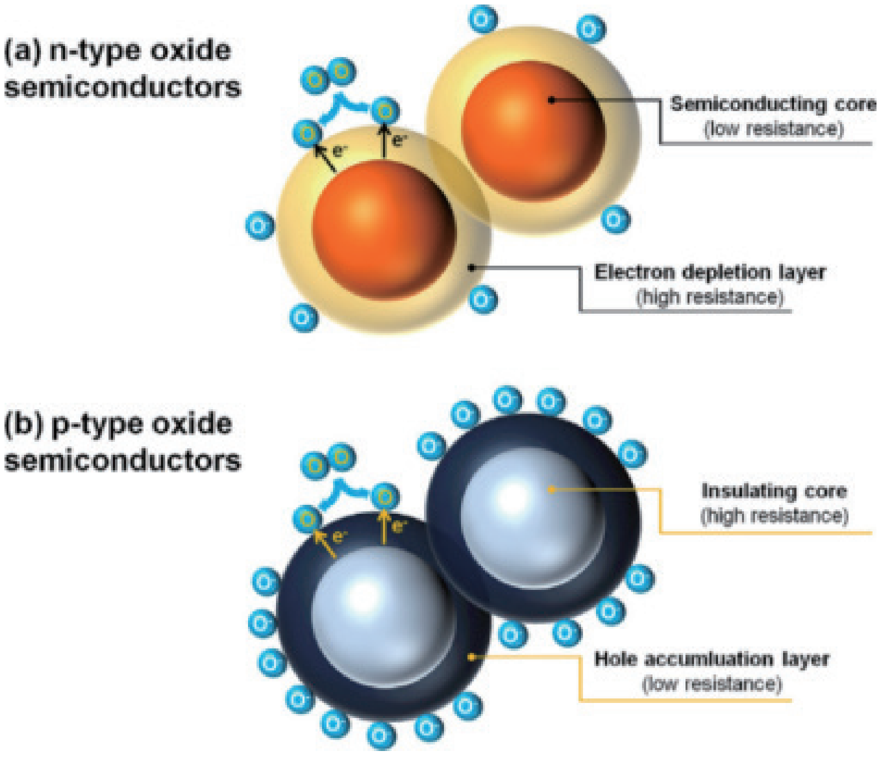

Fig. 1 Schematic diagram of core-shell structure of SMO: (a) n-type SMO; (b) p-type smo

2 preparation of SMO by hydrothermal method and microwave hydrothermal method

In recent years, semiconductor oxide (SMO) has attracted more and more attention because of its large band gap, high carrier mobility and low process temperature. There are many methods for preparing semiconductor oxides, such as hydrothermal method, microwave hydrothermal method, electrospinning method... Among them, hydrothermal synthesis method occupies the mainstream of semiconductor synthesis methods because of its high economic efficiency, simple operation, high purity of the product, good dispersion, and easy particle size control. In this chapter, we mainly talk about the preparation of semiconductor gas sensors by hydrothermal method and microwave hydrothermal method, and based on the detection of different gases to be measured, it is divided into two parts, namely, hydrothermal method and microwave hydrothermal method.

2.1 sensor preparation by hydrothermal synthesis

2.1.1 acetone gas sensor

Acetone can cause incalculable harm to personal safety and asset safety. Acetone vapor and air can form explosive mixture, which is easy to burn and explode in case of open fire and high heat, and can react strongly with oxidant. Its vapor is heavier than air, and can spread to a considerable distance at a lower place. It will catch fire and burn in case of fire source. In case of high heat, the internal pressure of the container increases, and there is a risk of cracking and explosion. In alkaline environment, when mixed with chloroform, explosion will occur. It is imperative to detect acetone. It has been reported that acetone gas sensors have been studied. Several typical examples will be discussed here.

Hydrothermal method is a common method to synthesize nano materials or micro materials with different morphologies by modulating the concentration of precursor solution. Yali Cheng et al. used this method to synthesize Fe2O3 with different morphologies through different concentrations of precursor solutions, assembled it into porous three-dimensional structure, and studied the effect of three-dimensional structure of Fe2O3 on the gas properties of acetone. At the optimal temperature of 220 ℃, the porous three-dimensional structure of Fe2O3 showed high sensitivity (52) and very short response / recovery time (8s / 19S) to acetone. As we all know, the more gas molecules adsorbed on the semiconductor surface, the better the sensitivity of the semiconductor. Due to the loose structure, the porous three-dimensional structure can promote the gas molecules to diffuse more rapidly and provide a larger specific surface area, which is conducive to the adsorption and desorption of gas molecules.

Alkareem et al. successfully prepared ZnO-CuO flower like heterostructures in the same way. ZnO-CuO flower like heterojunction is a p-n heterojunction formed at the interface between CuO and ZnO. Generally, when the ZnO nanostructured sensor is in the reducing gas, the negative oxygen adsorbed on the ZnO surface reacts with the reducing gas. The released electrons will return to the conduction band, causing the resistance to drop. In ZnO-CuO heterostructure, oxygen molecules carry electrons on CuO nanoparticles and exist as ions on ZnO-CuO surface. In acetone or isopropanol (reducing gas), electrons are released from CuO back to ZnO, resulting in the decrease of EDL. This is the reason why the resistance of ZnO-CuO flower heterostructure decreases. For different concentrations of acetone, such as 50ppm, 100ppm and 150ppm, the sensitivity of pure ZnO nanostructure was 13.02%, 20.21% and 43.06%, respectively, while the sensitivity of ZnO-CuO heterostructure was 14.19%, 24.34% and 54.96%, respectively. The improvement of sensing performance may be attributed to the increase of specific surface area and active adsorption sites.

Although TiO2 is a sensitive material which is less concerned, it has its unique advantages, such as low cost, high band gap energy and good chemical stability. F. J.stadler et al. prepared a sensor with a very low detection limit for acetone, and synthesized TiO2 nanoparticles by hydrothermal method. At the working temperature of 270 ℃, when the concentration of acetone is 1000ppm, the response time and recovery time are 10s and 9s, respectively, because the oxygen ions generated by the reaction with acetone molecules release electrons into the conduction band of TiO2, resulting in increased conductivity. In addition to the above examples, other sensors with excellent gas sensing performance for acetone gas are summarized in Table 1.

Table 1 Comparison of gas sensing performance of SMO based acetone sensor

SMO	Morphology	Conc.(ppm)	T（℃)	Resp.	Res. (s)	Rec.(s)	Ref.
WO_3/SnO_2	NA	600	360	26	Na	Na	[14]

NiO/SnO_2	NA	50	300	20.18	2	9	[15]
$CoFe_2O_4$ / SiO_2 / In_2O_3	Microsphere	10	260	13	1	59	[16]
$CuFe_2O_4$/α-Fe_2O_3	NA	100	275	14	~6	~70	[17]
Ce/In_2O_3	Microsphere	200	250	41.80%	2	154	[18]
Sb/In_2O_3	Microstructure	50	240	64.3	8	27	[19]

Note: Na:Not Available;

2.1.2 other VOCs gas sensors

With the progress of science and technology and economic development, people pay more and more attention to the interior decoration, and the decoration has become more and more complex. While the indoor environment has been beautified, the indoor pollution has become more serious. After the decoration of new houses, the main indoor pollutants (VOCs) will continuously volatilize over time. Indoor air pollution will cause "pathogenic building syndrome" (BBS), which will lead to dizziness, nausea, difficulty in concentrating and other symptoms, affecting human health. Here we will discuss three representative examples, the first is ethanol gas sensor, the second is formaldehyde gas sensor and the last is xylene gas sensor.

Zhu et al. synthesized zinc oxide nanoflowers by a simple hydrothermal method. Compared with ZnO nanoparticles and nanoplates, ZnO nanoflowers have the best gas sensing performance for ethanol. When the ethanol concentration reached 400ppm and the working temperature was 350 ℃, the response value of the gas sensor based on ZnO nanoflowers was 30.4, the response time was 10s and the recovery time was 4S. This is because the nanoflower structure has a larger specific surface area, and the three-dimensional nanoflower structure can provide a lot of space for the diffusion of ethanol molecules, so the response time is shorter.

Zhang et al. prepared mesoporous In2O3 nanoparticles by a simple, template free, low-cost hydrothermal method. The sensitivity of mesoporous In2O3 nanoparticle based gas sensor to 100ppm formaldehyde gas is 20 (working temperature is 280 ℃), and the response time and recovery time are 4S and 8s respectively, showing excellent gas sensing performance. This is due to the existence of a large number of pores in the mesoporous sensing materials, which is conducive to the gas diffusion in SMO materials, and also provides a large number of active sites for the adsorbed oxygen ions and formaldehyde gas.

Gao et al. prepared WO3-NiO material by template free hydrothermal method and made it into a gas sensor. Among them, the sensor based on 10at% WO3-NiO shows good xylene gas sensing performance and ultra-low detection limit (1.5-50ppb, xylene). This may be attributed to the large specific surface area, which makes more oxygen anions adsorbed on the surface participate in the oxidation reaction as much as possible, causing greater resistance changes, so that the sensor based on 10at% WO3-NiO shows good xylene gas sensing performance. Table 2 summarizes the sensors with superior performance for other VOCs gases except acetone.

Table 2 Comparison of gas sensing performance of SMO based sensor

SMO	Morphology	Conc.(ppm)	T (℃)	Resp.	Res. (s)	Rec. (s)	Ref.
Co /In_2O_3	Nanorod	10	130	Na	60	120	[23]
NiO/ZnO	NA	100	200	26.2	Na	Na	[24]
MoS_2/In_2O_3	NA	50	RT	75.2%	14	22	[25]
NiO/SnO_2	NA	1	100	3.3	Na	Na	[26]

Ni / SnO_2	Nanoparticle	1	200	9.9	18	10	[27]
Ga/ SnO_2	NA	50	230	95.8	3	39	[28]
In_2O_3 / ZnS	Microsphere	100	260	11.7	21	34	[29]
α-Fe_2O_3/$LaFeO_3$	Nanoparticles	100	240	10.1	1	5	[30]
Al / ZnO	Nanoplate	100	370	90.2	1.6	1.8	[31]
SnO_2/CoO	Nanorod	100	250	13.5	2-3	Na	[32]

Note: Na:not available;

2.2 Sensor preparation by microwave hydrothermal synthesis

Microwave hydrothermal synthesis of metal oxide has been recognized by more and more researchers, making it the first choice of sensitive materials for gas sensors. G. Neri et al. successfully prepared nano tungsten oxide (WOx) nanoparticles by MAH method. According to the tungsten oxide obtained by microwave radiation at different times, the sensors based on tungsten oxide are called S10, S20 and S30 respectively. S10 sensor has the best response to 100ppm ethanol, the response value is about 8.5, and the response time is 10s, showing good selectivity to the harmful gases mixed together. This may be because the S10 sensor has a larger specific surface area.

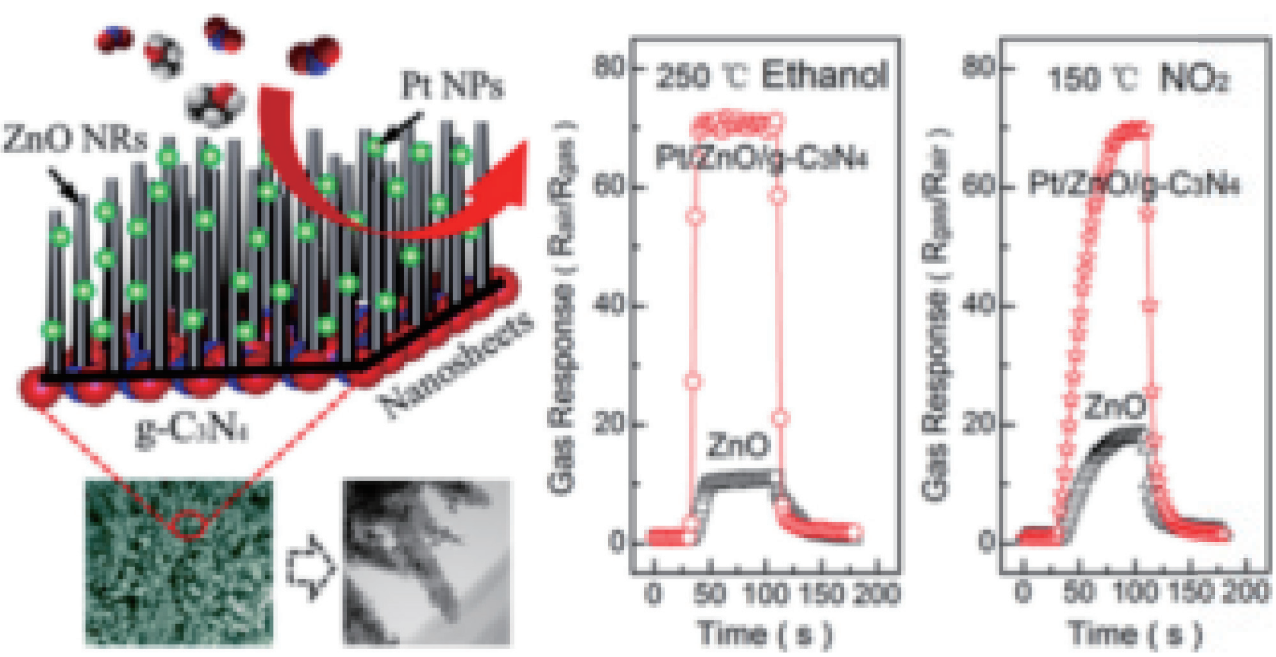

Fig. 2 Schematic diagram of Pt/ZnO/ g-C3N4 and gas sensitivity of sensor to ethanol and NO_2

Tian et al. first used the microwave hydrothermal method to grow evenly arranged ZnO nanorods on g-C3N4 nanosheets, and then deposited Pt nanoparticles on them by deposition method. Finally, Pt/ZnO/ g-C3N4 nanostructures were obtained (as shown in Figure 3). The Pt / ZnO / g-C3N4 nanostructured sensor has significant sensitivity, selectivity and response recovery time for ethanol and NO2 air pollutants. The gas sensing mechanism may be that the Pt / ZnO / g-C3N4nanostructure promotes the transfer of more electrons and consumes more gas molecules on the material surface, which improves the gas sensing response; It may also be that the difference between the maximum value of valence band and the minimum value of conduction band between ZnO and g-C3N4causes the separation of electron hole pairs and enhances the gas sensing performance of the sensor.

3 Summary

This paper focuses on the successful synthesis of various materials by hydrothermal and microwave hydrothermal methods. Among many synthetic methods, hydrothermal method has the advantages of economical efficiency and convenient operation. Its disadvantage is low efficiency, part of the heat energy is wasted, resulting in uneven heating. Compared with the hydrothermal method, the microwave hydrothermal synthesis method has the advantages of uniform solution heating, high efficiency, saving time and controlling the morphology of materials. However, neither the oxide prepared by microwave hydrothermal method nor hydrothermal method is the focus, they are only the process flow. In the field of gas sensing, more attention should be paid to the gas sensing performance of SMO gas sensors. Therefore, in order to improve the gas sensing performance of gas sensors, researchers have made many attempts, such as noble metal doping of sensing materials; Morphological changes; Heterojunction formation, etc.

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