

Research progress on Nano-Tungsten oxide gas sensors

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Abstract: In the field of research on the detection of various harmful gases, nano-semiconductor metal oxide gas sensors hold a very important position. As an n-type semiconductor metal oxide, tungsten oxide has become a research focus and hotspot in gas-sensitive materials in recent years due to its unique structural and performance characteristics. This paper briefly introduces the gas-sensing response mechanism of tungsten oxide-based gas-sensitive materials, summarizes the main processes and directions for improving the gas-sensing performance of nano-tungsten oxide materials in recent years, and finally points out its own shortcomings and future research and development directions.

Keywords: Nanomaterials, Tungsten Oxide, Gas Sensors

1. Introduction

In the fields of industrial production and environmental monitoring, the continuous improvement of people's requirements for production and detection has led to significant progress in the detection of harmful, toxic and other atmospheric pollutant gases. As an important tool for gas detection, gas sensors are widely used in various fields of work and life, providing an important guarantee for human life and production activities.

Gas sensors are sensors that detect target gases using detection methods such as electrochemical methods, optical methods, and electrical methods [1]. Among them, semiconductor metal oxide gas sensors detect target gases through changes in volt-ampere characteristics, conductivity, and surface potential caused by surface adsorption or reaction between the gas-sensitive element and the target gas, which are characterized by carrier movement. Semiconductor nano-metal oxide gas sensors are a research focus in the field of semiconductor metal oxide sensors because they have unique advantages. Firstly, the nano-metal oxide gas-sensitive materials used in such sensors have a large specific surface area, providing a large number of channels for gases; secondly, the scale characteristics of nano-materials also further reduce the size of the sensors. Currently, zinc oxide [2], tin oxide [3], titanium oxide [4], tungsten oxide, etc., are widely used. Among them, nano-tungsten oxide has attracted widespread attention due to its excellent physical and chemical properties [5]. Tungsten oxide is widely used in the detection of gases such as carbon oxides [6], hydrogen sulfide [7], ammonia [8], hydrogen [9], and ethanol [10].

This paper focuses on introducing the working mechanism and characteristics of tungsten oxide gas sensors, elaborates on the methods to improve their gas-sensing performance through regulating material preparation conditions, doping, modification, and other means, and briefly summarizes the shortcomings of tungsten oxide as well as its future development trends.

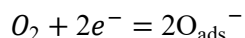
2. Principle of Gas-Sensing performance of tungsten oxide

Tungsten oxide is an n-type semiconductor metal oxide material. Its resistivity changes with the concentration of gases adsorbed on the surface, and it is sensitive to oxidizing or reducing gases (such as H₂S, H₂, NO₂, etc.) [11]. Therefore, it can be used as a material for sensors to detect these gases.

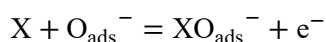
At present, the widely recognized gas-sensing mechanism of tungsten oxide is the adsorption-desorption model [12]. This model refers to the change in the electrical properties of the gas-sensing material caused by the adsorption or desorption reactions of the monitored gas on the surface of the material, thereby achieving

the purpose of gas detection. Generally, the operation of semiconductor metal oxide gas sensors is attributed to oxygen adsorption on the surface. The oxygen adsorbed on the surface first attaches to the material surface in the form of physical adsorption. At low temperatures, oxygen exists on the surface of tungsten oxide in the form of O_{2ads}^- . As the temperature rises, oxygen is converted into O_{ads}^- and O_{2ads}^- , and gradually, O_{ads}^- accounts for a larger proportion.

The reaction that occurs is:



In this process, electrons transfer from the interior of oxygen atoms to the surface, causing a deviation from electrical neutrality between the interior and surface of tungsten oxide as a gas-sensing material. The induced spatial electron layer triggers energy band bending. The reduction in the number of carriers on the material surface caused by the spatial electron layer leads to a decrease in its electrical conductivity. When a certain reducing gas X is present in the ambient atmosphere, the adsorbed oxygen will undergo a reaction:



The two reactions release one electron, thereby increasing the conductivity of the gas-sensing material. The two reactions proceed in opposite directions, and when the concentration of the detected gas is constant, they reach a dynamic equilibrium, thus enabling the detection of the measured gas.

Here, Figure 1 shows a schematic diagram of the surface reaction of tungsten oxide after the introduction of the detected gas.

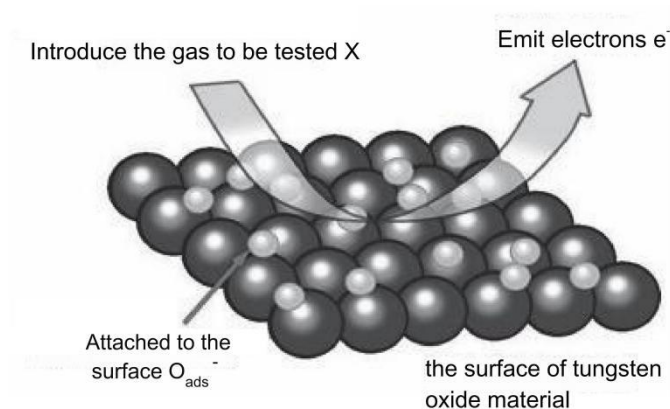


Figure 1 Schematic diagram of surface reaction of tungsten oxide after introduction of the detected gas

As tungsten oxide is an n-type semiconductor material, its resistance increases when reacting with oxidizing gases such as oxygen and nitrogen oxides, and decreases when reacting with reducing gases such as hydrogen, hydrogen sulfide, and ammonia. The corresponding situations are shown in Figure 2. The resistance change affects the voltage change in the test circuit (as shown in Figure 3), making it possible to measure the gas-sensing performance of tungsten oxide materials. Currently, the commonly used tubular gas-sensing elements are shown in Figure 4. In the experiment, nano-tungsten oxide gas-sensing materials are coated on the surface of the elements and connected to the circuit for detection.

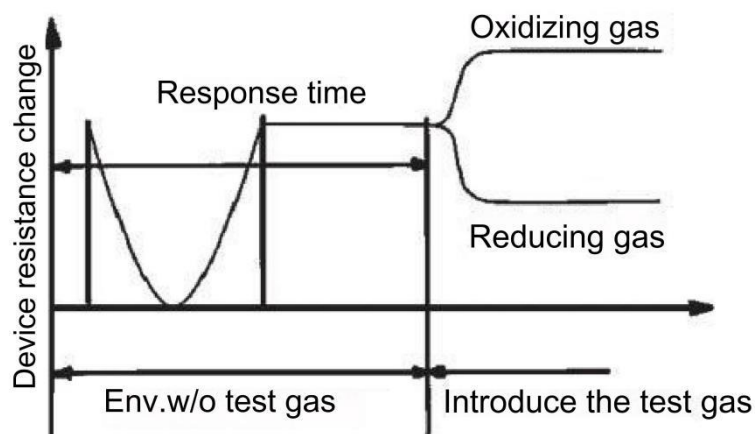


Figure 2 Schematic diagram of the response of gas-sensing elements

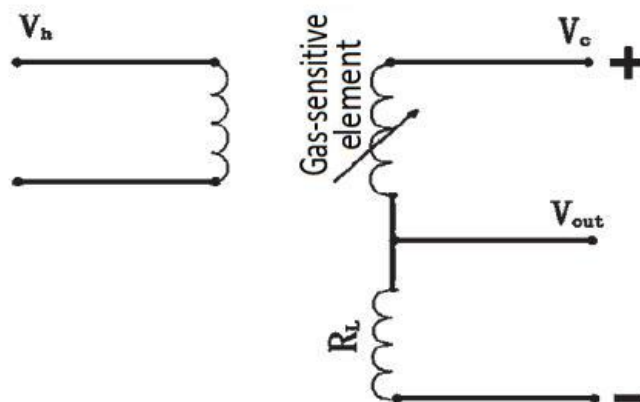


Figure 3 Circuit diagram of gas-sensing test

3. Research progress of Nano-Tungsten oxide gas sensors

In recent years, research on the gas-sensing performance of tungsten oxide has become a hotspot in this field. Most studies mainly focus on improving the gas-sensing performance of materials by controlling their morphology, structure, and doping with different elements. The following will mainly introduce the preparation and properties of several common nano-tungsten oxide materials.

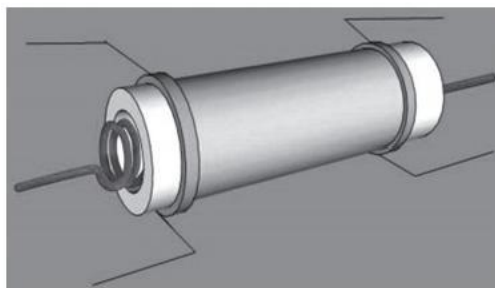


Figure 4 Tubular gas-sensing test electrode

3.1. Preparation of Nano-Tungsten oxide gas-sensitive materials with different structures

Regarding the results of regulating the morphology and structure of nano-tungsten oxide, current research has achieved the synthesis of zero-dimensional morphologies (such as nanoparticles), one-dimensional and two-dimensional morphologies [13-14] (such as nanorods, nanowires, nanobelts, nanosheets, etc.), and complex morphologies [15-17] (such as hollow spheres, flower clusters, urchin-like structures, etc.). The synthesis methods include physical and chemical methods.

For tungsten oxide materials with complex morphologies, such as hollow spherical tungsten oxide materials, due to their structural characteristics, gas can enter the interior of the hollow spherical structure through the gaps on the spherical surface, thereby having more opportunities to contact the material surface, so their gas-sensing performance is significantly improved. Chong Wang et al. synthesized and calcined hollow spherical tungsten oxide by hydrothermal method [16]. It can be seen from the SEM and TEM images in the paper that the diameter of such hollow spheres is about 1 μm , the thickness is about 150–300 nm, and they are self-assembled by irregularly shaped nanoparticles with obvious gaps between the particles. This material has very good selectivity and sensitivity to nitrogen dioxide gas. At a test temperature of 100 $^{\circ}\text{C}$, the sensitivity to nitrogen dioxide gas with a concentration of 1 ppm is significantly higher than that to gases such as Cl_2 , CO, and H_2S . When the NO_2 concentration is 50 ppb, the sensitivity reaches about 50; and when the NO_2 concentration reaches 400 ppb, the sensitivity is close to 300.

The increase in specific surface area can greatly improve the gas-sensing performance of the material. The reason is that the increase in specific surface area enables the surface of the gas-sensing material to adsorb more oxygen in the gas-sensing reaction and convert the oxygen into oxygen ions [17]. Urchin-like and flower crown-like tungsten oxide materials have relatively large specific surface areas, so they have good sensitivity to specific gases. Tian ming Li et al. used potassium sulfate as the reaction precursor and sodium tungstate as the reactant, and adjusted the pH value with hydrochloric acid to prepare urchin-like tungsten oxide with a diameter of about 3 μm and nanostructures [18]. The optimal gas-sensing response temperature of this material is 300 $^{\circ}\text{C}$, and it still shows good response and recovery speed when the minimum H_2S concentration is 100 ppm. Zhenyu Wang et al. prepared flower crown-like tungsten trioxide gas-sensing materials by microwave hydrothermal method [19]. The grown flower crowns are 30–40 nm in thickness and 300–400 nm in length. At a test temperature of 90 $^{\circ}\text{C}$, the sensitivity to NO_2 gas with a concentration of 40 ppm is 42; at a test temperature of 300 $^{\circ}\text{C}$, the response and recovery times of the gas-sensing element to NO_2 gas with a concentration of 100 ppm are 1 s and 6 s, respectively.

3.2. Performance optimization of Nano-Tungsten oxide gas-sensing materials

In the process of application, the various limitations of traditional tungsten oxide gas-sensing materials have prompted people to explore various methods to improve their gas-sensing performance. Among them, the most widely used methods are doping the materials [20], modifying them, or compounding them with other materials [21].

Substances doped in tungsten oxide nanomaterials mainly improve the gas-sensing performance of tungsten oxide materials by inhibiting crystal growth, exerting catalytic effects, or permeating into the structure of tungsten oxide. Currently, the main dopants are noble metals and rare earth elements.

The doping of noble metals mainly plays a role in catalysis and inhibiting crystal growth. At the same time, the introduction of noble metals (such as Pd, Pt, etc.) [22-25] can also reduce the energy barrier for gas adsorption and desorption, making tungsten oxide materials doped with noble metals exhibit excellent properties such as high sensitivity and high response-recovery speed. Daling Chen et al. used tungsten oxide gas-sensing materials doped with silver nanoparticles [26]. At a test temperature of 150 $^{\circ}\text{C}$, the sensitivity to NO gas with a concentration of 0.5 ppm was 15, and the sensitivity to NO gas with a concentration of 10 ppm even reached 344; the response speed of the material was the fastest at 150 $^{\circ}\text{C}$, about 5–10 s, while its recovery speed peaked at 250 $^{\circ}\text{C}$, about 30 s.

When tungsten oxide materials are processed by compounding with other materials (such as polythiophene, graphene, etc.) [27-30], the resulting composites show better performance than either of them alone as gas-sensing materials. Some reduce the reaction temperature, some significantly improve gas sensitivity, and some composites have better selectivity for specific gases. The polyaniline-tungsten oxide composite nanomaterials developed by Shin Koo et al. [31] were prepared into films through a fiber

spinning process, and their gas-sensing performance was then studied. This composite-structured gas-sensing material shows good gas-sensing response speed and excellent selectivity to hydrogen at room temperature. Compared with other gas-sensing materials that need to be heated to work, this room-temperature working gas-sensing material can not only reduce energy consumption but also is convenient to use, and exhibits a longer service life because it does not need to be heated.

4. Shortcomings and Development directions

4.1. Shortcomings of tungsten oxide Gas-Sensing materials

As a semiconductor metal oxide gas-sensing material, tungsten oxide has its unique advantages, but it also has some shortcomings. Firstly, the selectivity of tungsten oxide gas-sensing materials is not excellent; secondly, some materials have high requirements for test temperature; finally, tungsten oxide gas-sensing materials are greatly affected by the environment. Therefore, research on tungsten oxide gas-sensing materials needs to be further developed.

4.2. Development directions of gas-sensing materials

Based on the various deficiencies mentioned in the above introduction, gas-sensing materials still need to further improve their performance to meet the requirements for detecting target gases in production and daily life. The development of gas-sensing materials mainly proceeds in the following directions.

4.2.1. *Discovery of new materials*

The application of nano-scale single crystal materials, mesocrystalline materials, and composite materials [32] in gas sensors has gradually come into people's vision. These new materials have broad development prospects and will become the focus and hotspot of research on gas-sensing materials in the future.

4.2.2. *New prep.Processes & Performance optimization*

Other nano-material preparation processes, such as atomic layer deposition and magnetron sputtering, are introduced into traditional preparation processes. In terms of optimizing the process of gas-sensing materials, the current widely used methods are doping with various atoms or functional groups, modifying the material surface, and composite nano-materials also make good contributions to optimizing the gas-sensing performance of materials.

4.2.3. *Research on arrayization and intellectualization of gas sensors*

In-depth research on the arrayization of gas sensors will provide more room for the mass production and even large-scale application of gas sensors. Intelligence is the overall direction of the next technological development, and the development of gas sensors is also inevitable.

5. Conclusion

Tungsten oxide nanomaterials have received continuous attention due to their extensive applications in the field of gas-sensing research. By controlling the morphology, crystal form, or adopting various improvement processes, people have further enhanced the gas-sensing performance of tungsten oxide. However, there are still many deficiencies in the practical application of tungsten oxide nano gas-sensing materials in production and daily life, such as insufficient selectivity and stability, and the inability of mass production to meet industrial requirements. Therefore, it is necessary for people to continue in-depth exploration in these aspects, so that they can serve people and society more conveniently and widely.

6. References

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