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Research on Metal Oxide Semiconductors in Gas Sensors

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Abstract

This paper mainly introduces the classification of metal oxide semiconductor gas sensors, the research status of metal oxide semiconductors and the improvement methods of metal oxide semiconductor gas sensors.

Keywords

Gas Sensors; Metal Oxide Semiconductors.

1. Introduction

With the increasing environmental pollution and the strengthening of environmental governance, the frequent occurrence of safety production accidents and terrorist attacks, and the increasing requirements for miniaturization, intelligence, multi-function and low power consumption of gas sensors, semiconductor metal oxide gas sensors have ushered in a rare development opportunity, but they are also faced with the challenges of scientific and technical problems such as the lack of clear sensitive mechanism, the lack of optimal design of sensitizing materials, the high power consumption, and the difficulty in taking into account selectivity and response value. Therefore, it is necessary to further strengthen the research on the sensitive mechanism of gas sensors to provide theoretical support for the optimal design of sensitive materials.

2. Overview of Metal Oxide Semiconductor Gas Sensors

The emergence of gas sensors began in the 1930s when Brauer P. et al. found that the electrical conductivity of metal oxide Cu_2O changes with the adsorption of water molecules [1]. Since then, researchers have gradually conducted more in-depth research on sensing materials and sensitive mechanisms. In the 1950s, Heiland first reported that ZnO could be used as a sensitive material, and studied the effect of electrical conductivity before and after the gas contacted the surface of the material [2]. In 1962, Seiyama and Kato fabricated a chemical resistance type gas sensor device with a ZnO thin film as the sensitive layer, which can detect various gases such as hydrogen by detecting the change in the conductivity of the device in different gas environments. The development of oxide-based gas sensors has laid an important foundation [3]. In 1968, the founder of Figaro (FIGARO) company, Taguchi Naoyi invented the semiconductor SnO_2 gas sensor for the first time [4]. This marks the transition of metal oxide-based gas sensors from theoretical to practical stage, and is an important milestone in the development history of semiconductor sensors. Then, in order to broaden the sensitive material system of gas sensors, different n-type, p-type and composite metal oxide materials have been successively studied and reported.

3. Metal Oxide Semiconductor Gas Sensor Classification

There are many types of semiconductor gas sensors. According to the interaction site between semiconductor and gas, they can be divided into surface control type and volume control type. Surface control means that most of the chemical reactions occur on the surface of the material,

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and then the signal transmission is realized through physical conduction. The research is more in-depth and widely used. The reaction site of the volume-controlled gas sensor is inside the material, and it is often used for the detection of alcohol and oxygen; in addition, according to the physical properties of semiconductor changes, it can be divided into two types: resistance type and non-resistance type. Resistive semiconductor gas sensors use the resistance change of semiconductor materials when contacting gas to detect gas composition or concentration, and have the characteristics of relatively low cost, small device structure and simple preparation process; non-resistive semiconductor gas sensors are Through the adsorption and reaction of the gas, some characteristics of the gas are changed to realize the direct or indirect detection of the gas, such as the use of the volt-ampere characteristics of the diode or the change of the threshold voltage of the field effect transistor. According to different device heating methods, it can also be divided into two categories: direct heating and bypass heating. The structure of the direct heating gas sensor is shown in Figure 1.1[5]. This type of device integrates the heating circuit and the test circuit in the inside of the gas-sensing material has the advantages of low production cost, small device size, and simple preparation process. However, since the two parts of the circuit are covered in the test material, it is inevitable that mutual signal interference will occur, resulting in a significant reduction in measurement accuracy. Correspondingly, the bypass heating device completely separates the test circuit and the heating circuit, which cleverly solves the problem of direct heating. At present, such devices can be divided into planar and tubular structures according to their morphology, as shown in Figure 1.2 and Figure 1.3[5,6]. The planar structure is mainly based on alumina ceramics, with a heating circuit embedded inside, and the surface is constructed for testing. Electrode, the test material is grown to the surface of the test electrode to form a sensitive layer, so that the two circuits are completely separated, which improves the stability and anti-interference ability of the device, but the heating layer of this structure is greatly affected by the cost, high-cost high-quality The heating circuit of the gas sensing element has a wide layout, and the device is heated evenly. However, for most devices, there are few heating circuits, which often causes uneven heating of the device and affects the performance of the material. The other structure, the tubular device shows its superiority in this part. The inner Ni-Cr heating wire covers the entire Al_2O_3 ceramic tube, so that the device is heated evenly. There are two circles of Au electrodes on the outer surface of the ceramic tube. There are two Pt wire pins on each electrode for soldering the test circuit. This kind of device mainly coats the gas-sensitive material on the outer surface of the test gold electrode, so as to achieve the purpose of separating different circuits, and this kind of device generally bears a large amount of heat, which reduces the influence of airflow on the material, and can improve the repeatability and reliability of the device. It is stable, but due to its cylindrical structure, it is difficult to grow in situ on the surface, so it is usually applied to powder materials that can be coated.

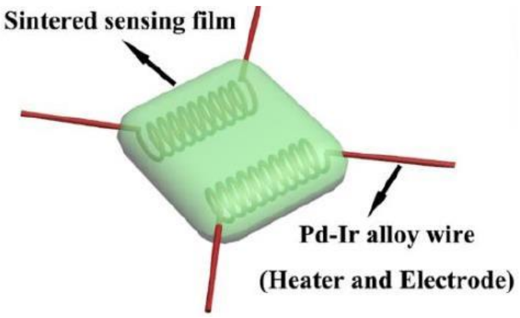

Figure 1.1 Schematic diagram of the structure of the direct heating gas sensor

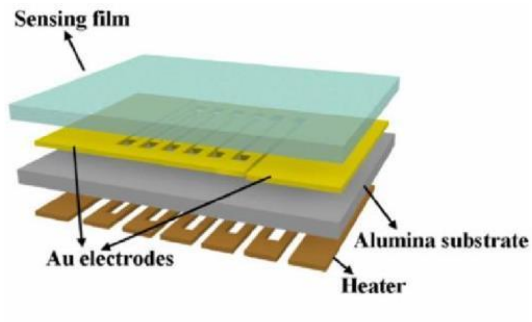

Figure 1.2 Schematic diagram of the structure of the planar gas sensor

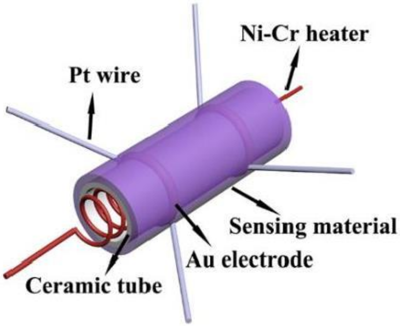

Figure 1.3 Schematic diagram of the structure of the tubular gas sensor

4. Research Status of Metal Oxide Semiconductor Gas Sensors

Metal oxide refers to a compound composed of oxygen element and one or more metal elements, wherein the multiple elements contained are in the same metal oxide phase, rather than a simple mixture or complex of multiple metal oxides. Since metal oxides have been proved to be good gas sensing materials, the research on sensitive materials is mainly based on binary oxides, such as n-type metal oxides: ZnO, SnO_2, WO_3, α-Fe_2O_3, etc., p-type metal oxides Compounds: Co_3O_4, NiO, CuO, Mn_3O_4, etc. [7-13], but there are few studies on multi-component metal oxides.

4.1. Binary Metal Oxide Semiconductor Gas Sensor

Binary metal oxide refers to a binary compound composed of a metal and oxygen elements. Zeng Y et al[14] fabricated a micro structured CO sensor based on a layered porous ZnO nanosheet thin film by a two-step liquid phase method. The sensor exhibits high response to CO (25 s response time) and low cross-response to common interfering gases at an operating temperature of 300 °C. Patil D et al [15] synthesized Co_3O_4 nanorods (about 6–8 nm in diameter and 20-30 nm in length) by calcining hydroxycarbonate in air by coprecipitation/digestion method and studied their CO gas sensing properties. Co_3O_4 nanorods exhibit excellent CO gas sensing properties: high sensitivity (6.55 for 50ppm CO at 125°C), fast response (3~4s), fast recovery (5~6s) and good repeatability, selectivity and lower operating temperature (~250°C).

4.2. Multi-Element Metal Oxide Semiconductor Gas Sensor

Multi-component metal oxides not only have the advantages of binary metal oxides, but also have the advantages of abundant multi-valence cations, unique crystal structure characteristics, and controllable composition. They are very potential gas sensing materials. At present, among the reported multi-component metal oxide material systems, oxides with perovskite structure (ABO_3) and spinel structure (AB_2O_4) are the main ones [16].

4.2.1. Multicomponent Metal Oxide Semiconductors with Perovskite Structure

Perovskite-structured oxides (ABO_3, where A and B are metal ions) are one of the most studied multicomponent metal oxides. Perovskite-structured metal oxides have two metal cations of different sizes and different valences, making them very suitable as a bulk material for doped or controlled defect states. In the field of gas sensing, the modification strategy of perovskite-type materials is very flexible, and gas sensors constructed with perovskite-type oxides also show very good gas sensing properties.

Sun et al. prepared perovskite-structured $La_{1-x}Ba_xFeO_3$ (x≤0.3) by sol-gel method [17]. The results showed that the growth of the material grain size was suppressed with the increase of Ba^{2+} concentration, and the resistance and ethanol gas-sensing properties of the $La_{1-x}Ba_xFeO_3$ based sensor had a strong correlation with the Ba^{2+} concentration. For $LaFeO_3$, the carriers are holes generated by the ionization of La^{3+} ion vacancy defect $[VLa_x]$. When Ba element is doped, La^{3+} in $LaFeO_3$ is replaced by Ba^{2+}, and the ionization of $[BaLa_x]$ will also generate holes. Due to the high doping amount of Ba^{2+} in the experiment, the concentration of $[BaLa_x]$ will be greater than $[VLa_x]$, which leads to the increase of the conductance of the material and the decrease of the basic resistance (x≤0.1). However, if the doping amount of Ba^{2+} continues to increase, more oxygen vacancies will be generated in the material, and some holes will be neutralized by electrons, which will lead to an increase in resistance (x>0.1). When the sensitivity performance of ethanol gas is studied, the sensitivity performance of the sensor based on $La_{0.75}Ba_{0.25}FeO_3$ is the best, and the response to ethanol gas (500ppm) can reach 172 (240℃). Ba^{2+} doping causes a stoichiometric deviation in $LaFeO_3$ and enhances the surface defect concentration. When x = 0.25, the surface defect content reaches the maximum, which creates a more active surface state for oxygen adsorption, so the sensitivity of the sensor is the highest. In some research reports, perovskite-structured materials are also used as chemical sensitizers to improve the gas-sensing properties of composites. For example, Kang et al. used perovskite $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ to decorate SnO_2 nanofibers ($LSCM@SnO_2FITs$) with tube-and-sleeve morphology, and used it to construct a gas sensor to detect formaldehyde gas [18]. The as-synthesized LSCM has a higher concentration of oxygen vacancies and a larger work function (LSCM: 6.80 eV, SnO: 4.55 eV), which can significantly promote oxygen escape and surface electron loss of SnO. The gas-sensing test results show that the SnO_2 nanofibers loaded with LSCM have a very high response to formaldehyde, and the sensitivity to 5ppm formaldehyde can reach 26.5 with good selectivity. This composite sensitive material is expected to be applied in real-time monitoring of indoor air quality.

4.2.2. Spinel-Structured Multicomponent Metal Oxide Semiconductors

Compounds of spinel structure (AB_2O_4, in which A and B are metal ions) In spinel-type oxides, cation A is in the +2 or +4 valence state, and correspondingly, the cation B is in the +3 or +2 valence state, which can be expressed as $A^{2+}B_3{}^{+2}O_4$ and $A^{4+}B_2{}^{+2}O_4$. Due to the diversity of structures and cations, there are many internal defects, such as intrinsic defects: Schottky defects, Frenkel defects and some interstitial defects.

Andris Sutka et al. prepared $Ni_{1-x}Co_xFe_2O_4$ (x=0, x=0.01, x=0.05, x=0.1) by a sol-gel method. After the material was calcined at 800 °C for 1 h, it was rapidly cooled by quenching in water and slowly cooled at room temperature (2.5 °C/min) two methods for cooling treatment [19]. It is found that the $NiFe_2O_4$-based sensor has a higher response to acetone gas when x=0, and the sensitivity increases with decreasing cooling rate. The characterization results by XPS show that a slower cooling rate (2.5 °C/min) can form a higher concentration of Ni^{2+} on the surface of the material. Ni^{2+} on the surface of nickel ferrite is the active site for oxygen chemisorption, which can promote the effective reaction between acetone and the material surface, while the introduction of cobalt will replace the more active Ni^{2+} and limit the conduction function of the sensor material. Srashti Jain et al. synthesized $CuCo_2O_4$ nano disks by hydrothermal method, and in the preparation process, excessive amounts of Cu and Co were made in this spinel structured oxide, respectively, which regulated the stoichiometric ratio of the two transition metal elements [20]. The study found that when the material Co is excessive, the sensor constructed with it shows good response and recovery characteristics to ammonia at room

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temperature and 57% RH, but it is difficult to recover to hydrogen sulfide and nitrogen dioxide, and hardly responds to carbon monoxide. In the material, Cu element exists in the form of Cu^{2+}, Cu^{2+} is a kind of interface acid, Co element exists in the form of Co^{3+}, which is a hard acid, and the reducing gas ammonia is hard alkali. According to the hard-soft acid-base (HSAB) theory, hard acid preferentially reacts with hard base, therefore, Co^{3+} sites are more likely to react with ammonia gas than Cu^{2+}, which explains the reason why the material is more sensitive to ammonia gas when Co is excessive.

4.2.3. Multiple Metal Oxides of other Structures

In addition to perovskite and spinel-structured multi-component metal oxides, other multi-component metal oxides have also been studied as sensitive materials in the field of gas sensing. For example, Tong et al. reported a p-type delafossite structure (ABO_2) $CuCrO_2$ sensitive material, which can generate a large number of single ionized oxygen vacancy defects ($V_O\cdot$) in the material through vacuum annealing [21]. These oxygen vacancies can provide coordinatively unsaturated sites (CUSs) to facilitate the adsorption of gas molecules, which greatly improves the sensitivity to ethanol gas. Li et al. prepared a monoclinic scheelite-phase $BiVO_4$ porous film using a single-layer colloidal crystal as a template, and the pore size can be adjusted to 1000, 500 and 200 nm [22]. The $BiVO_4$ material with a pore size of 200 nm exhibits good gas-sensing properties to hydrogen sulfide, with a sensitivity of 18.9 to 25 ppm hydrogen sulfide at 75 °C, and the detection limit can be as low as 62.5 ppb. Zhang et al. prepared Mo-Bi composite metal oxide $MoO_3/Bi_2Mo_3O_{12}$ with more complex material system and structure by solvothermal method [23]. The sensitivity of $MoO_3/Bi_2Mo_3O_{12}$ with hollow spherical morphology to 50 ppm trimethylamine is 25.8, which is higher than that of pure MoO_3 (10.8) and $Bi_2Mo_3O_{12}$ (4.8), and has good selectivity. The larger specific surface area of the material and the formation of the heterointerface are the main reasons for the improvement of the gas sensing performance of the sensor based on $MoO_3/Bi_2Mo_3O_{12}$.

5. Metal Oxide Semiconductor Gas Sensor Modification Method

At present, the research on sensitive materials mainly focuses on: 1. Morphological structure design and construction of sensitive materials; 2. Functional modification of sensitive materials (hetero ion doping modification); 3. Multi-component composite heterostructures and precious metal decoration,).

5.1. Morphology and Structure Control

The particle size, dimension, microscopic morphology and internal structure of the material will directly affect the sensitivity, response recovery time and other characteristics of the gas sensor. Therefore, researchers design sensitive materials into different morphological structures to improve the utilization of materials. In addition to zero-dimensional nanoparticles, other dimensional structures such as one-dimensional nanowires, nanotubes, two-dimensional nanosheets, nano disks, and three-dimensional materials with different geometrical and hierarchical structures have also been designed and synthesized. Firooz AA et al. [24] synthesized nanoflower-like SnO_2 by a surfactant-assisted hydrothermal method. The nanoflower-like SnO_2 sensor has excellent CO gas sensing performance, its sensitivity to 1000 pm CO at 275 °C is 1217, and the response and recovery time to 50 pm CO at this temperature are 1.5 s and 30 s, respectively.

5.2. Heterogeneous Ion Doping

Due to the different valence states, gas adsorption and catalytic properties of different metal cations, it is possible to flexibly select cations to occupy different lattice sites to design sensitive materials. Through the selective substitution of cations at A/B sites in multi-component metal oxides ($A_xB_yO_z$), gas sensors can exhibit different gas sensing properties. For example, Niu et al.

synthesized spinel-structured ZnM_2O_4 (M=Fe, Co, and Cr) materials and found that the sensitivity of chlorine gas changed with the different metal cations at the B site. The order of sensitivity to chlorine gas from large to small is: $ZnFe_2O_4$>>$ZnCo_2O_4$>$ZnCr_2O_4$[25]. In addition, the cation at the B site in the perovskite structure also plays an important role in the gas sensing performance, which can significantly affect the perovskite oxide semiconductor properties [26]. Haron et al. successfully synthesized nanostructured perovskite oxide $LaMO_3$ (M=Al, Co and Fe) by co-precipitation method, and studied the ethanol sensing properties and sensing mechanism [27]. The sensors based on $LaAlO_3$ exhibited n-type semiconductor characteristics and higher response to ethanol, while the sensors based on $LaFeO_3$ and $LaCoO_3$ materials exhibited p-type semiconductor characteristics and lower response. For $LaFeO_3$ and $LaCoO_3$, the p-type semiconducting properties are related to the mixed valence states of B-site cations (Fe^{3+}/Fe^{2+} or Co^{3+}/Co^{2+}). The replacement of B^{2+}-B^{3+} cations generates a large number of hole carriers in the material, the density of which is much higher than that of electrons induced by oxygen vacancies. For $LaAlO_3$ with an almost ideal perovskite configuration, oxygen atoms are easily overflowed from the lattice at high temperature, which will make the material as a whole exhibit n-type semiconductor characteristic. Generally speaking, the mobility of holes is less than the mobility of electrons, so the sensing capability of p-type semiconductor oxides is generally lower than that of n-type semiconductor oxides. In addition, the smaller grain size and higher porosity of the LaAlO3 material in this experiment also led to its higher sensitivity to ethanol. T. Zhang et al [28] prepared hollow nanostructured Er, La, Yb-doped In_2O_3 by using carbon spheres as templates, and realized the selective response to ethanol in the presence of cyclohexane, acetone, xylene, methanol and NO_2.

Therefore, the sensing properties of multi-element metal oxides will largely depend on the elemental composition type of different sites, and the sensitivity to specific gases can be improved by cation replacement of the material.

5.3. Multicomponent Composite Heterojunctions and Noble Metal Decoration

In semiconducting metal oxides, the recombination of multiple components forms a heterojunction, and electrons adjust the material carrier concentration, the width of the depletion layer, and the barrier height of the interface through the interaction between the Fermi level and the energy band, thus changing the physicochemical properties of semiconductor materials [29]. For multi-element metal oxide semiconductors, the combination of n or p-type semiconductor oxides to construct novel heterojunctions (p-n, n-n and p-p) is an effective strategy to improve the gas sensing properties of materials. For example, Bai et al. achieved efficient detection of formaldehyde by modifying n-type $ZnSnO_3$ graded microspheres with p-type NiO nanosheets [30]. Due to the difference in work function, the majority carriers in the two materials will diffuse in opposite directions until the Fermi level of the whole system is balanced. At the same time, a depletion layer will be formed at the interface between $ZnSnO_3$ and NiO, which will increase the basic resistance of the sensor. When formaldehyde gas diffuses to the surface of the material, electrons flow into the material system to increase the carrier concentration of the material and decrease the resistance. The whole process makes the sensor based on NiO@$ZnSnO_3$ p-n heterogeneous materials highly sensitive to formaldehyde gas. Chesler P et al [31] prepared SnO_2-ZnO mixed oxide ceramics by wet method. The sample with SnO_2(50mol%)-ZnO(50mol%) composition has a response time of ~60s to 5ppm CO at a working temperature of 500℃, a recovery time of 15min, and it shows good selectivity to methane and propane cross response test.

Doping materials with noble metal catalysts (Au, Ag, Pd, Pt, etc.) can also help to improve the gas sensing performance of multi-element metal oxide-based gas sensors. The introduction of noble metal catalysts can greatly reduce the reaction activation energy, which can not only increase the response of the gas sensor to the target gas, but also increase the reaction rate and

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shorten the response/recovery time. The mechanism of action of noble metals is mainly explained from the point of view of electronic sensitization and chemical sensitization [32]. Electron sensitization mainly refers to the formation of noble metal oxides after the noble metal is partially oxidized, and acts as an electron acceptor to extract electrons from the host material to form a depletion layer at the material interface. When exposed to a reducing gas environment, electrons are reinjected from the noble metal oxide back into the host material, thereby enhancing the sensitive response to the target gas. Chemical sensitization mainly refers to the "overflow effect" of the noble metal element, that is, the noble metal dissociates to the oxygen anion, and the oxygen anion overflows and adsorbs to the surface of the material. By increasing the material activity and reducing the reaction activation energy, the adsorption and reaction of gas molecules are promoted. Thereby lowering the operating temperature, increasing the response/recovery rate, and increasing the sensitivity [33]. Synthesized Pd-modified SnO_2 nanostructures by a one-step microwave-assisted hydrothermal method. The results show that the SnO_2 modified with 3.0wt% Pd has the best performance in the response test to 100pm CO at 100℃. Bhardwaj N et al [34]. synthesized Ag-SnO_2 nanocomposite thin films by combining vapor deposition method based on thermal evaporation with thermal annealing, which exhibited excellent CO gas sensing properties, including high sensitivity, fast response recovery and good selectivity to CO gas.

6. Summary

As semiconductor metal oxide sensors are more and more widely used in environmental monitoring and medical diagnosis, their higher detection limit, poor selectivity, higher operating temperature and stability (baseline drift phenomenon) are urgently needed to be solved. main problem. Therefore, the application research of gas sensor needs deep excavation. Whether it is the design of materials or the research of sensitive properties, the purpose of the sensor is to make the sensor more efficient and practical in application. There is also a lack of related simulation and testing of sensor application in the existing work. In future work, we will continue to explore the application potential of sensors in the fields of environmental monitoring and disease diagnosis and treatment.

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