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Mini Review

Some Metal Oxide Semiconductors Thin Films applied in Gas Sensor Applications

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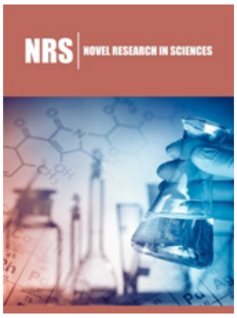

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Abstract

This mini review focuses on the application of N and P-type metal oxides semiconductor thin films, such as TiO_2, SnO_2, CO_3O_4 and Mn_3O_4, used in air pollution for NO_2 and H_2S gas sensing applications. Metal Oxide thin films exhibit several advantages including a higher catalytic effect, low humidity dependence, and improved performance. However, the sensing performance of metal oxide thin films is strongly related to their intrinsic physicochemical properties of the materials. A review of each comparison, as well as metal oxide that has the high gas sensitivity in the recent years. Future trends to overcome the challenges of metal oxide semiconductors gas sensors are also presented.

Keywords: Metal oxide; Semiconductors; Thin films; Air pollution; Gas sensors

Introduction

In recent years, the alarming increase in environmental pollution has necessitated the development of effective and efficient monitoring systems to detect and mitigate the impact of various pollutants and harmful gases on our planet. As a result, gas sensors have emerged as vital tools for detecting and quantifying the presence of pollutants in the atmosphere.

This mini-review focuses on gas sensors based on metal oxides, a category of sensors that has garnered significant attention due to their performance and versatility in detecting a wide range of gases. As the concentration of pollutants in the atmosphere continues to rise, understanding the operation and potential of metal oxide-based gas sensors becomes crucial for addressing environmental concerns and ensuring the well-being of our planet.

The Earth's atmosphere is composed of a complex mixture of gases, each playing a critical role in maintaining a stable and habitable environment. However, the introduction of various pollutant gases, such as Carbon Monoxide (CO) [1], Nitrogen Dioxide (NO_2) [2], Sulfur Dioxide (SO_2) [3], Sulfur Hydrogen (H_2S) [4] and volatile organic compounds (VOCs) [5], has led to significant environmental challenges. These pollutants are primarily generated by industrial activities, transportation, agriculture, and other human-related sources.

Among the array of pollutants, Hydrogen Sulfide (H_2S) and Nitrogen Dioxide (NO_2) have emerged as significant contributors to environmental degradation. These two gases, though distinct in their origin and chemical properties, share a common characteristic: their capacity to exert a substantial influence on the natural world. In this context, it becomes essential to explore and comprehend the profound effects of H_2S and NO_2 on the environment, encompassing the air we breathe, ecological ecosystems, and public health. This examination not only deepens our understanding of the intricacies of environmental pollution but also underscores the urgency of developing robust gas detection and mitigation strategies.

Metal oxide-based gas sensors, with their unique properties and capabilities, have emerged as valuable tools in this endeavor.

In the subsequent sections of this mini-review, we will explore the principles of operation, key advancements, and applications of metal oxide-based gas sensors. By delving into the realm of thin films gas sensing technology, we aim to shed light on their pivotal role in NO_2 and H_2S detection and contribute to a better understanding of their potential in safeguarding the planet.

Principle of Resistive Metal Gas Sensors

Resistive metal oxide gas sensors operate based on the change in electrical resistance when exposed to target gases. These sensors consist of a sensing material, typically a metal oxide semiconductor, which exhibits variable electrical conductivity in the presence of specific gases. When the sensor comes into contact with the target gas, a chemical reaction occurs at the surface of the sensing material. This reaction results in a change in the number of charge carriers (electrons) within the material, which, in turn, causes a measurable change in electrical resistance. The degree of resistance change is directly proportional to the concentration of the target gas, allowing for the detection and quantification of specific gases in the environment. These sensors are widely used in gas detection and air quality monitoring applications due to their simplicity, sensitivity, and responsiveness to various gases Figure 1.

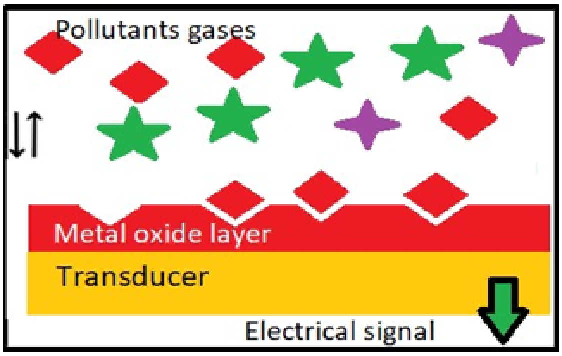

Figure 1: General mechanism of gas detection for gas sensor-based metal oxide.

Metal Oxide Materials

Metal oxides are chemical compounds composed of a metal element bonded to oxygen. They are formed when a metal reacts with oxygen, typically through oxidation processes. Metal oxides can have various chemical and physical properties depending on the specific metal involved and the oxidation state of the metal. The two types of conductivity found in metal oxide materials, namely, “N-type” and “P-type” conductivity, and their impact on gas detection.

In this review, we will examine the outstanding performance characteristics of metal oxide materials, including TiO_2, SnO_2, CO_3O_4, and MN_3O_4 [6-14], as they pertain to H_2S and NO_2 gas sensors.

Metal oxide N-type

N-type (negative-type) conductivity in metal oxide materials is associated with the presence of excess electrons. This excess of electrons is typically introduced through the incorporation of dopant atoms, which have more electrons than the host metal. In N-type materials, these dopants are often elements from Group V of the periodic table (e.g., nitrogen or phosphorus), which contribute extra electrons to the crystal lattice.

N-type semiconductor materials, such as TiO_2, SnO_2, and other suitable materials, are characterized by excess electrons and high electron density [15-20].

For H_2S detection: When exposed to H2S, an n-type semiconductor’s excess electrons are readily captured by H_2S molecules. This capture results in an increase in electron concentration in the material. As a consequence, the material’s electrical conductivity increases (decrease in resistance) when H_2S is present. Therefore, N-type semiconductors are highly sensitive to H_2S and are suitable for its detection.

For NO_2 detection: N-type semiconductors, due to their high electron density, are less sensitive to NO_2, which is an oxidizing gas. The increased electron density in the n-type semiconductor can inhibit its interaction with NO_2, leading to limited sensitivity to this gas.

Metal oxide P-type

P-type (Positive-Type) conductivity in metal oxide materials is associated with the presence of electron “holes.” These holes are vacancies in the crystal lattice where an electron could exist. P-type conductivity is typically achieved by doping with elements from Group III of the periodic table (e.g., boron, aluminum), which have fewer electrons than the host metal.

P-type semiconductor materials, such as CO_3O_4 and MN_3O_4 are characterized by electron holes (vacancies) and lower electron density.

For NO_2 detection: When exposed to NO_2, which is an oxidizing gas, a p-type semiconductor’s electron holes readily interact with NO_2 molecules. This interaction results in the acceptance of electrons from NO_2, causing a decrease in electron hole concentration. As a result, the material’s electrical conductivity decreases (increase in resistance) in the presence of NO_2. Therefore, p-type semiconductors, including MN_3O_4, are well-suited for the detection of NO2 due to their sensitivity to oxidizing gases.

For H_2S detection: P-type semiconductors are less sensitive to reducing gases like H_2S since the presence of electron holes can hinder interactions with H_2S. To effectively detect H_2S, n-type semiconductor materials or composite sensors that combine n-type and p-type materials may be used.

The following table provides a concise overview of the sensing performance of N-type and P-type semiconductors concerning their reactivity to reducing and oxidizing gases (Table 1). This comparison sheds light on their respective sensitivities [21,22].

Table 1: Some examples of sensing performance of N and P-type towards reducing and oxidizing gases.

Materials	Conductivity-Type	Gas	Operating Temperature (°C)	Concentration (ppm)	Sensitivity of N or P-type Respectively (Ra/Rg) or (Rg/Ra)	Reference
TiO_2	N	NO_2	500	100	3.5	[15]
		H_2S	300	100	6	[16]
SnO_2	N	NO_2	100	100	5.36	[17]
		H_2S	180	100	25.3	[18]
Co_3O_4	P	NO_2	250	100	1.3	[19]
		H_2S	300	100	5.4	[20]
Mn_3O_4	P	NO_2	23	100	0.62	[21]
Co_3O_4 / SnO_2	P-N	NO_2	150	100ppm	90	[22]

Future Trends in Gas Sensors Field

Nanowires, nanorods, nanobelts, and nanofibers, among other One-Dimensional (1D) nanostructures, have recently garnered significant interest for their potential to improve chemical sensing capabilities. Among these, nanowires, in particular, have been a focal point of research in recent years. The exceptional characteristics of metal oxide nanowires, including their elevated aspect ratios, substantial surface-area-to-volume ratios, exceptional crystallinity, remarkable thermal stability, efficient carrier-charge transport, robust chemical stability, and compatibility with electronic systems, position them as a promising option for developing gas sensors [23].

Conclusion

The N or P type of metal oxides thin films, such as TiO_2, SnO_2, Co_3O_4 and Mn_3O_4 their efficiency in gas sensor applications were reviewed [24].

In summary, the type of semiconductor material chosen for gas detection plays a critical role in determining the sensor's sensitivity to specific gases. N-type materials are highly sensitive to reducing gases like H_2S due to their excess electrons, while P-type materials are effective in detecting oxidizing gases like NO_2 because of their electron hole interactions. The proper selection and combination of these materials enable the accurate detection of both H_2S and NO_2 gases in various environments.

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