Screening and Array Optimization of Metal-Oxide-Semiconductor Gas Sensing Materials

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Abstract. Metal-Oxide-Semiconductor (MOS) based gas sensor is considered to be a promising method for harmful gas detection, but the detection usually needs to meet the conditions of excellent selectivity, high responsivity, quick response, low power consumption, low detection concentration limit, etc. To improve the performance of the sensor, materials need to be screened and array need to be optimized. This paper will briefly introduce the research on MOS gas sensing materials screening and array optimization.

1. Introduction
The ecological environment problem has always been the focus of people's attention. In the face of environmental deterioration and environmental emergencies, it is urgent to improve the ability to prevent all kinds of environmental emergencies, especially the detection ability of toxic and harmful gases. The research on the methods and equipment for rapid and effective detection of toxic and harmful gases is the focus of scientific research. MOS gas sensor is a widely recognized detection method. To achieve efficient detection, the sensor should have the advantages of fast response, high responsivity, low power consumption, good reliability, low price, long service life, and convenient use. Therefore, it is very important to enhance the responsivity and selectivity of the gas sensor. The overall performance of the MOS gas sensors can be effectively improved by a further screening of MOS gas sensing materials and optimization of sensor array.

2. Metal oxide semiconductor gas sensing materials
MOS gas sensing materials mainly use the reaction of oxygen adsorbed by metal oxide semiconductor and target gas molecules to cause the change of resistance, to change the conductivity and other parameters to achieve the purpose of detection. In 1962, Siyama¹ and other scholars from Kyushu University of Japan used semiconductor metal oxides for gas-sensitive detection, opening up a new field of gas sensor materials. Subsequently, scholars began to study n-type and p-type MOS gas sensing materials. The common n-type semiconductors are SnO₂, WO₃, ZnO, Cr₂O₃, Fe₂O₃, In₂O₃, TiO₂, etc, and the common p-type semiconductors are CuO, NiO, FeO, MnO₂, etc.

Although the MOS gas sensors have the advantages of fast response and high responsivity, there are still some shortcomings in the selectivity and stability. Therefore, as the key to affect the sensing performance, MOS sensing materials need to be further screened and optimized to strengthen the weak performance in some parameters.
3. Screening of metal oxide gas sensing materials

3.1 Screening method of MOS gas sensing materials---combinatorial material technology method

In order to simplify the tedious repetitive material screening experiment, scholars have studied the combinatorial material science method, which originated from Kennedy's idea of simultaneous synthesis and characterization of sample materials in 1965,[2] and was initially applied to Hanak's multi-sample material research on superconductors in 1970.[3] Hanak thought that the traditional trial and error method used at that time was time-consuming and laborious, and it would cost a lot of manpower, material, and financial resources to find new materials. Therefore, he proposed the idea of parallel synthesis and analysis of multiple samples, that is, the original form of the combination method. However, due to the limitation of early technology, the research of new materials in this field has not made progress in the past 20 years.

Until the 1980s, this "multiple sample concept" method, which combines raw materials for parallel analysis, was successful in the screening of small molecule drugs, resulting in "combinatorial chemistry". Using this method, the cost of synthesizing a precursor by biochemists at that time was much lower than that by traditional methods, and its research cost was about 0.16% of the past, saving thousands of dollars, and the synthesized precursor was nearly 830 times in the past. The research of biochemists gives new hope to the field of materials science.

In 1995, Xiang Xiaodong et al. Applied a new type of integrated material chip in the research of high-temperature superconducting materials, and they achieved success.[4] This experiment initially realized the idea of composite materials, improved the traditional trial and error method, and established the important position of composite material chip technology in composite materials science. This method soon played an important role in the screening of superconducting materials,[5][6] giant magnetoresistance materials,[7][10] amorphous metal alloy materials,[11] fluorescent materials,[12][15] and semiconductor materials.[16][18]

Combinatorial materials science is a method of combining different materials on the same substrate, and characterizing the specific properties of these combined products, which can be used to screen new materials or further explore. Different from the traditional synthesis and characterization of single materials, this method can quickly find new compounds, improve the screening efficiency of new materials, facilitate the establishment of the corresponding material database, and open up ideas for new research directions. Although this method may not be efficient enough for a single sample, the overall efficiency can be greatly improved by avoiding a lot of repetitive and similar work, which is conducive to the screening and research of new materials.

The basic principle is shown in Figure 1, that is, two groups of different raw materials, a and B, can be combined to form A_iB_j at the same time. The m×n composite material products are integrated into the same substrate, and then the material products on the substrate are characterized at the same time, and finally screened.

![Figure 1 principles of combinatorial materials](image)
There are two major technologies in combinatorial materials science: parallel synthesis technology and high-throughput screening technology. The purpose of parallel synthesis is to integrate a large number of raw material samples in the same substrate so that the materials can form a material library under similar experimental conditions, reduce the repetition of similar experimental operations, and efficiently synthesize a large number of material samples for characterization and research. The parallel synthesis process can be realized by accurately transporting the micro reaction raw materials to the microreactor, or by directly controlling the chemical reaction in the microreactor. High-throughput screening technology is a technology that can quickly screen material sample library and test gas sensing performance after forming material samples.

With the development of technology, the above two combinatorial materials technologies are gradually combined with the information field, resulting in many new technologies and some branch technologies. Although combinatorial materials science is limited by the variety of materials and their properties, there are still some technical difficulties in the process of synthesizing composite materials. However, synthetic screening can maximize the complementarity of materials, change the defects of a single material, and make materials continuously updated and optimized. At present, the screening of semiconductor gas-sensitive materials is widely used.

3.2 Application of combinatorial material science method in semiconductor material selection

The performance of metal oxide semiconductor gas sensing materials is related to many factors, such as different element doping, different preparation process, different experimental environment. Therefore, it is necessary to establish a huge material library for research. The combinatorial material science method can greatly shorten the time of semiconductor material selection, improve the experimental efficiency and reduce the experimental cost.

Koplin[19] and siemons[20] initially carried out a high-throughput screening platform, prepared metal oxide nanomaterials by polyol method, and tested the surface modification of ZnO materials by doping Au, Ce, Ir, Pd, Pt, Rh, and Ru. Using multiple electrode substrates and high-throughput impedance spectroscopy (HT-IS), a wide range of materials can be screened in a short time.

Li D[21] et al. Modified the surface of SnO2, WO3, and ZnO System materials with 34 kinds of elements, and adjusted their working field by using light and heat modulation methods. They studied the gas sensing performance of the material membrane through a self-made high-throughput test platform, optimized and screened out the material array with the best performance.

Shen J L[22] prepared pure α-MoO3 and In2O3 materials, and doped α-MoO3 nanosheets with different concentrations of Ni. And in this project, In2O3 was doped with different concentrations of Al. They characterized these materials, tested formaldehyde and ethyl acetate gases, and screened the material with the best responsivity.

Zhang Q P[23] et al. prepared a room temperature photoexcited gas sensor based on ZnO material. The performance of the gas-sensitive material was optimized by field control, and the optimal material was screened. ZnO-Ag nanoparticles were prepared, and it was found that the gas sensor has a high responsivity for detecting NO2 gas excited by visible light at room temperature.

Wang Y Q[24] et al. prepared WO3-SnO2 binary surface modification system and various materials produced by SnO2–WO3–Co3O4 ternary composite system. Based on high-throughput technology, the prepared materials were characterized by the pump-suction odor analyzer network independently developed in the laboratory. The synthesized materials were compared and screened, and it was found that the gas sensitivity is closely related to the matrix material.

The ultimate purpose of material screening is to make gas-sensitive materials with excellent selectivity and responsivity to form an array sensor for simultaneous monitoring of a variety of harmful gases.

4. Optimization of metal oxide semiconductor gas sensor array

4.1 Significance of array optimization
After long-term development, the responsivity of a single gas sensor has reached a high level, but the selectivity is poor. At the same time, it is not in line with the objective reality to use hundreds or more gas sensors to measure an odor. The gas sensor array can solve these problems, but there is the problem of array optimization. Besides, Timothy\(^{25}\) reached the following conclusion through experiments: when all the sensors in the array are single class sensors, if the size of the array increases, the amount of effective information contributed by the sensor decreases, while the noise content remains unchanged. Therefore, there is an optimal array size in terms of Signal to Noise Ratio (SNR). To improve the detection performance of the sensor, it is particularly important to optimize the sensor array.

Although the more types of sensors and the stronger selectivity, the easier it is to improve the detection breadth and efficiency, it also increases the difficulty of system data processing, which may lead to "dimension disaster" in the future.\(^{25}\) Also, the more the number of array sensors, the more strict the requirements of the manufacturing process, and the production cost will increase, so it is difficult to achieve the goal of low price and easy to carry. Therefore, selecting the appropriate number of sensors to form a sensor array can optimize the analysis ability of gas sensors, reduce the workload of subsequent processing, and ensure the miniaturization of the whole system.

### 4.2 Method of array optimization

The first step is to construct the initial array. The sensors in the array should meet the following requirements: high sensitivity; comprehensive response to various components of the detected gas; good stability and repeatability; fast response and recovery. The initial array should choose sensors with different material systems and appropriate number.\(^{26}\) Of course, the preparation of gas sensing materials is the premise of forming the initial array, so starting from improving the performance of the sensors in the initial array, the optimization of the sensor array can also be better realized.

The second step of array optimization is to determine the final array. In this process, sensor information and array information need to be preprocessed. Sensor information preprocessing includes normalization, differentiation, etc.; array information preprocessing includes feature parameter selection and feature selection.\(^{27}\) Most of the commonly used array optimization methods focus on optimizing array information preprocessing. When choosing the characteristic parameters, it is usually possible to choose the following parameters:

- Static response parameters, such as the maximum value of the curve, the stability value, the difference between the maximum value and the minimum value over some time.
- Dynamic response parameters, such as the slope of the response curve, the average value over some time, the instantaneous value at a point in time.
- Parameter selection by combining dynamic and static information.\(^{28,29}\)

Feature selection is to select some of the most effective features from the initial feature parameters to form an optimal array. Because of the enormous amount of computational effort in artificial array optimization, some search strategies may be used in feature selection. The commonly used feature selection algorithms are generalized sequential forward algorithm, random search algorithm,\(^{30}\) genetic algorithm (GA), and simulated annealing algorithm (SA).\(^{31}\) The results of feature selection from different search strategies will also be different, so the selection of the algorithm should be based on the actual needs in array optimization. Optimizing sensor arrays plays an important role in increasing array selectivity and reducing power consumption.

### 5. Conclusions

MOS gas sensor is a promising gas detection method. To improve the performance of the sensor, the materials are usually screened and the sensor array is optimized. Combinatorial materials technology has been widely accepted by scholars in the field of material screening. Although there are still some technical problems in the process of synthesizing materials due to the limitation of the variety of materials and properties, it can screen materials efficiently. By optimizing the sensor array, the selectivity of the array can be increased and the power consumption of the array can be reduced.
However, if we want to better optimize the performance of the MOS sensor, we need to further explore the sensing materials and the response mechanism of the array.

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