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Review

Semiconductor metal oxide gas sensors: A review

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ABSTRACT

This review paper encompasses a detailed study of semiconductor metal oxide (SMO) gas sensors. It provides for a detailed comparison of SMO gas sensors with other gas sensors, especially for ammonia gas sensing. Different parameters which affect the performance (sensitivity, selectivity and stability) of SMO gas sensors are discussed here under. This paper also gives an insight about the dopant or impurity induced variations in the SMO materials used for gas sensing. It is concluded that dopants enhance the properties of SMOs for gas sensing applications by changing their microstructure and morphology, activation energy, electronic structure or band gap of the metal oxides. In some cases, dopants create defects in SMOs by generating oxygen vacancy or by forming solid solutions. These defects enhance the gas sensing properties. Different nanostructures (nanowires, nanotubes, heterojunctions), other than nanopowders have also been studied in this review. At the end, examples of SMOs are given to illustrate the potential use of different SMO materials for gas sensing.

1. Introduction

Detection and monitoring of flammable, toxic and exhaust gases are important for both energy saving as well as environmental protection [1,72]. Gas sensors have been in use for monitoring flammable as well as toxic gases in domestic and industrial environment [1]. The cheap, reliable, small and low power-consuming gas sensors are in great demand due to the wide range of applications. With the increasing demand for better gas sensors of higher selectivity and sensitivity, rigorous efforts are in progress to find more suitable material with required surface and bulk properties [13]. SMO gas sensors are generating interest as these materials fulfill the requirement of an ideal sensor to a very good extent.

Semiconductor metal oxide (SMO) gas sensors are the most investigated group of gas sensors [3] and recently the SMOs, having size in the range of 1 nm–100 nm, are being increasingly used for gas sensing due to their size dependent properties. Nanomaterials are unique because of their mechanical, optical, electrical, catalytic and magnetic properties. Apart from this, these materials also possess high surface area per unit mass. Further, new physical and chemical properties emerge when particles are in nanometer scale. The specific surface area as well as surface to volume ratio increase drastically when the size of the material decreases. Also, the movement of electrons and holes in semiconductor nanomaterials are affected by size and geometry of the materials [8]. High crystalline structure, ability of noble metal doping, and competitive production rate increase the demand of production for nanoparticles for gas sensors development [51].

This review article is focused on types of gas sensors and their comparison, factors affecting the sensitivity, selectivity and stability of SMO gas sensors, gas sensing mechanism of the above group of gas sensors. Furthermore the prospect of NH_3 sensing by different sensors are reviewed and compared with SMO gas sensors. Dopant or impurity induced variations which improve the properties of SMO materials for gas sensing applications is also being considered in this review.

2. Types of gas sensors

Over the past decades, many types of gas sensors have been developed based on different sensing materials and methods. Accordingly, the gas sensors are classified as catalytic combustion, electrochemical, thermal conductive, infrared absorption, paramagnetic, solid electrolyte and metal oxide semiconductor sensors [22]. Liu et al. [35] has classified the gas sensors based on their sensing methods and divided them to two groups: (a) methods based on variation in electrical properties and (b) methods based on variation in other properties. Materials like semiconductor metal oxides (SMO), carbon nanotubes and polymers are able to sense gas based on variation in electrical properties. The other variations are optic, acoustic, gas chromatographic and calorimetric. Comini [10] classified the gas sensors according to the measurement methods as (1) DC conductometric gas sensors (2) Field-Effect-Transistors (FET) based gas sensors (3) Photoluminescence (PL) based gas sensors. A comparison of various types of gas sensors is given in Table 1 and has been studied by Korotcenkov [29].

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Table 1
Comparison of various types of gas sensors [29].

Parameters	Types of Gas Sensors				
	SMO Gas Sensors	Catalytic Combustion Gas Sensors	Electro Chemical Gas Sensors	Thermal Conductivity Gas Sensors	Infrared Absorption Gas Sensors
Sensitivity	E	G	G	P	E
Accuracy	G	G	G	G	E
Selectivity	F	P	G	P	E
Response Time	E	G	F	G	F
Stability	G	G	P	G	G
Durability	G	G	F	G	E
Maintenance	E	E	G	G	F
Cost	E	E	G	G	F
Suitability to portable instru-ments	E	G	F	G	P

E: excellent, G: good, F: Fair, P: Poor.

Though there are many types of gas sensors available, but in this study the focus will be on SMO gas sensors.

3. Performance of gas sensors

The performance of gas sensors can be evaluated by different parameters like sensitivity, selectivity, response time, [29,35], reversibility or recovery time [23,7,35] fabrication cost and stability [35]. Sensitivity is the smallest volume concentration of the target gas that can be sensed in the time of detection. Sensitivity can be defined as Ra/Rg for reducing gases and Rg/Ra for oxidizing gases, where Ra is the resistance of the gas sensor in the reference gas (usually air) and Rg stands for resistance of the sensor in the target gas [23,65]. This is unit less parameter and percentage sensitivity is expressed by [(Ra − Rg)/Ra] * 100% [45]. Selectivity is the ability of the gas sensors to detect a specific gas in a mixture of gases. Response time is the period from the time when gas concentration reaches a specific value to that when a sensor generates a corresponding signal. Reversibility is whether a sensor returns to its original state when gas concentration returns to normal [35]. Recovery time is the time required for a sensor signal to return to its initial value after a step concentration change from a certain concentration value to zero. Stability is the ability of a gas sensor to reproduce results for a certain period of time. The result includes retaining the sensitivity, selectivity, response time and recovery time. An ideal sensor should possess high sensitivity, selectivity and stability, low response time and recovery time and low fabrication cost [7].

The performance of the different materials (SMO, Catalytic metal, Conducting polymers, Optical sensors) can be compared with respect to their response time, and lower detection limit for a particular gas. In this section a comparative study is done to evaluate the performance of

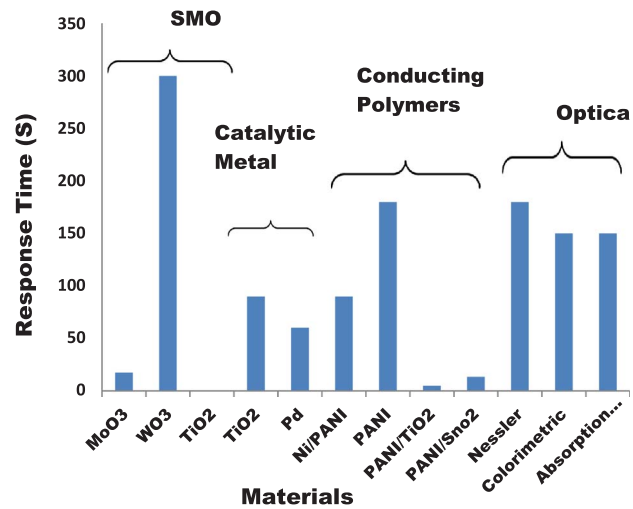

Fig. 1a. Comparison of different sensor materials according to their response time for NH_3 sensing [32,46,59,26,56,12,6].

SMO sensors with catalytic metal, conducting polymers and optical sensors, based on Ammonia (NH_3) sensing. NH_3 is included in this study as it is a natural gas that is present in the atmosphere in relatively low concentration of ppb or sub-ppb levels. Recently, most of the NH_3 is emitted by human activity. One of the major sources of NH_3 emission is combustion from chemical plants and motor vehicles. NH_3 sensors are used in food technology, chemical plants, medical diagnosis and environmental protection [46]. There are many ways to detect NH_3. High concentrations are easily detectable by penetrating odors. Gas sensors are required to determine lower concentration of NH_3. NH_3 sensors are applicable in automotive industry, chemical industry like fertilizer industry, refrigeration systems especially in ammonia production plant. NH_3 sensors are required in medical applications also. Measuring breath ammonia levels can lead to faster diagnostics for patients with urea imbalance due to different diseases [59]. Table 2 shows the requirement for NH_3 gas sensors in different application areas. Figs. 1a and 1b shows the comparison of different sensor materials with respect to their response time and lower detection limit for sensing ammonia (NH_3) gas and Figs. 2a and 2b show the comparison of different sensor materials with respect to their response time and working temperature, respectively, at different lower detection limits for ammonia (NH_3) gas sensing.

4. General properties of semiconductor metal oxide (SMO) used for gas sensing

The properties of SMOs can be divided into two groups according to the operating temperature which dictates the mechanism by which these materials function. The two groups are: (1) materials which follow surface conductance effects and (2) materials which follow bulk conductance effects. The first group of oxides operates at lower

Table 2
Requirements for ammonia gas sensors in different application areas [59].

Application		Detection limit	Required response time	Temperature range(°C)
Environmental	Monitoring ambient condition	0.1 ppb to > 200 ppm	Minutes	0–40
	Measure in stable	1 to > 25 ppm	~1 min	10–40
Automotive	NH_3 emission from vehicle	4- > 2000 g/min (conc. Unknown)	Seconds	Up to 300
	Passenger cabinet air control	50 ppm	~1 min	0–40
	NH_3 slip	1–100 ppm	Seconds	Up to 600
Chemical	Leakage alarm	20 to > 1000 ppm	Minutes	Up to 500
Medical	Breath analysis	50–2000 ppb	~1 min	20–40