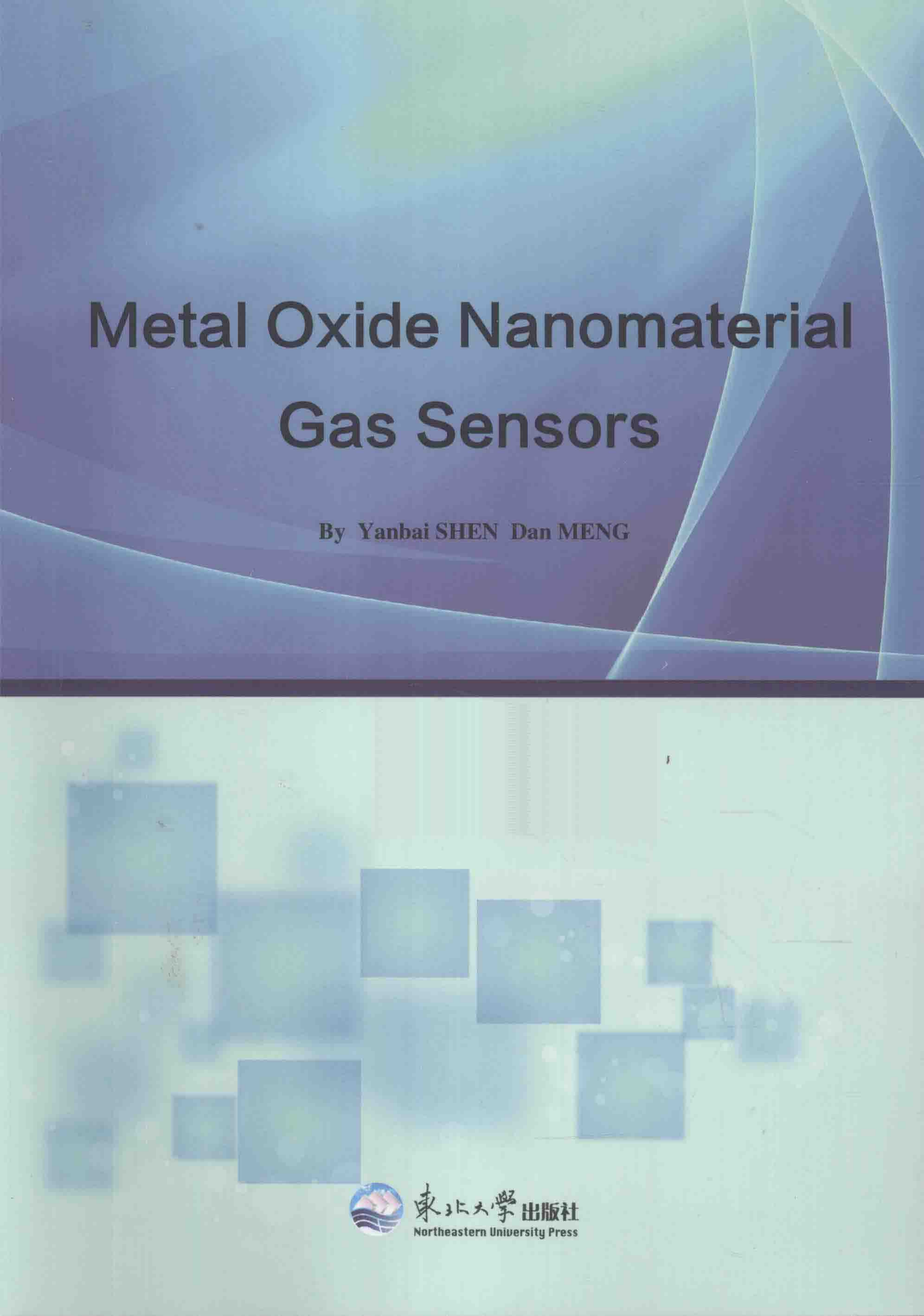
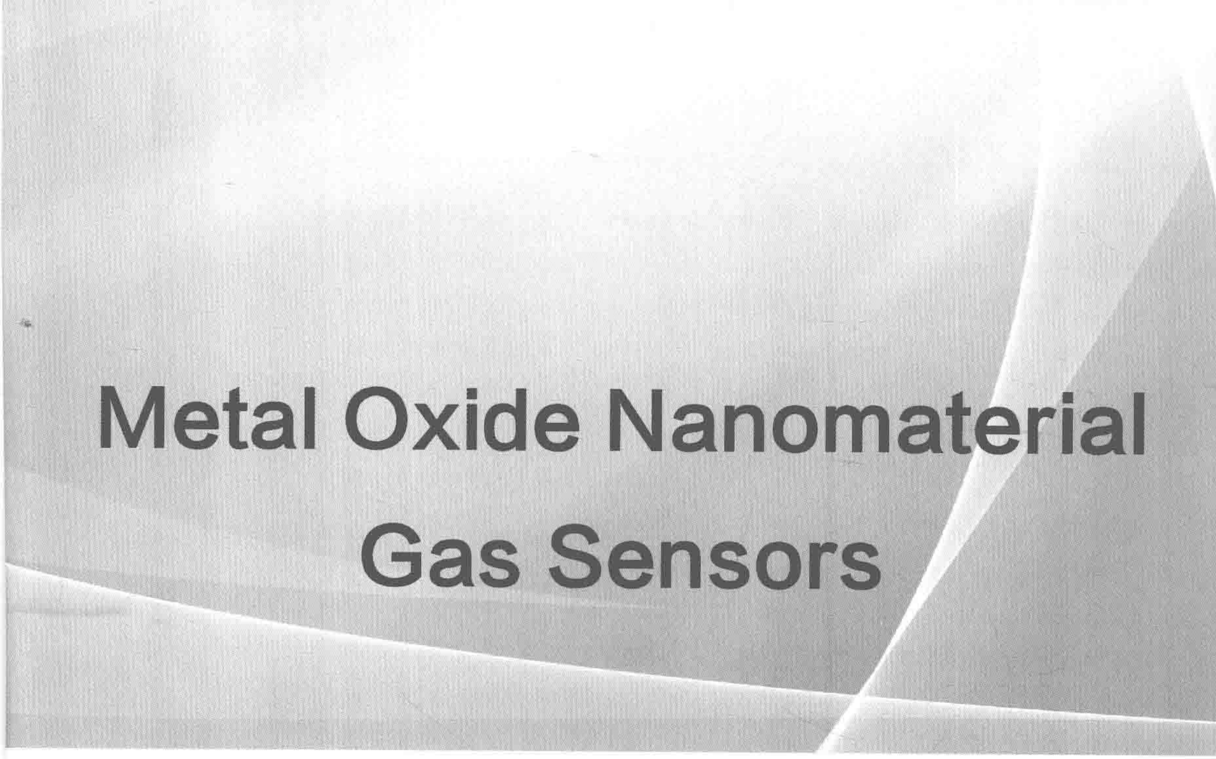


Metal Oxide Nanomaterial Gas Sensors

By Yanbai SHEN Dan MENG

東北大學出版社
Northeastern University Press



Metal Oxide Nanomaterial Gas Sensors

东北大学出版社
·沈 阳·

图书在版编目（CIP）数据

金属氧化物纳米材料型气体传感器 = Metal Oxide Nanomaterial Gas Sensors：英文 / 沈岩柏，孟丹著．—沈阳：东北大学出版社，2014. 11
ISBN 978－7－5517－0816－6

Ⅰ. ①金…　Ⅱ. ①沈…　②孟…　Ⅲ. ①氧化物—金属材料—纳米材料—应用—气体—传感器—研究—英文　Ⅳ. ①TP212

中国版本图书馆 CIP 数据核字（2014）第 242998 号

出 版 者：东北大学出版社
地址：沈阳市和平区文化路3号巷11号
邮编：110819
电话：024—83680267（社务室）　83687331（市场部）
传真：024—83680265（办公室）　83680178（出版部）
网址：http：//www. neupress. com
E-mail：neuph@neupress. com
印 刷 者：抚顺光辉彩色广告印刷有限公司
发 行 者：东北大学出版社
幅面尺寸：170mm × 240mm
插　　页：4
印　　张：11. 5
字　　数：301 千字
出版时间：2014 年 11 月第 1 版
印刷时间：2014 年 11 月第 1 次印刷
组稿编辑：孙　锋
责任编辑：方　璐　潘佳宁
责任校对：图　图
封面设计：刘江旸
责任出版：唐敏志

ISBN 978－7－5517－0816－6　　定　　价：45. 00 元

Dan Meng

Dan Meng was born in Tieling County, Liaoning Province, China, in 1979, and lives in Shenyang City now. Dan Meng received her PhD from Toyama University of Japan in 2010 and then worked as a postdoctoral researcher at Toyama University of Japan from 2011 to 2012. Now, she is working as a lecturer in the College of Chemical and Engineering at Shenyang University of Chemical Technology, China.

The research fields of Dan Meng are mainly focused on the structural, electrical and gas sensing properties of oxide semiconductor materials, and preparation of polymer nanomaterials and their application in gas sensor and coating.

Until now, Dan Meng has published 14 academic papers, in which 11 papers are indexed by SCI, and 1 paper is indexed by EI. The highest IF of a single paper is 4.814, and the total value of IF is more than 29. From the SCI database, it is found that the published papers have been cited more than 260 times, and the highest citation is over 75 times for a single paper. To date, she has attended the domestic and international conferences 6 times.

Yanbai Shen

Yanbai Shen was born in Mishan County, Heilongjiang Province, China, in 1978, and lives in Shenyang City now. Yanbai Shen received his PhD from Toyama University of Japan in 2009 and then worked as a postdoctoral researcher at Nagoya University in Japan until 2012. Now, he is working as an associate professor in the College of Resources and Civil Engineering at Northeastern University, China.

The research fields of Yanbai Shen are mainly focused on preparation and structural characterization of oxide semiconductor nanomaterials, development of high-performance gas sensors based on oxide semiconductor nanomaterials, development and application of proton conductors to intermediate-temperature fuel cells, development and application of high-performance diesel particulate matter sensors, and mineral materials. At present, Yanbai Shen is the editor of International Journal of Metals. He is the member of Chinese Instrument and Control Society, Catalysis Society of Japan, The Electrochemical Society of Japan, The Japan Society of Applied Physics.

Until now, Yanbai Shen has published over 90 academic papers, in which 30 papers are indexed by SCI, 42 papers are indexed by EI. The highest IF of a single paper is 13.734, and the total value of IF is more than 110. From the SCI database, it is found that the published papers have been cited more than 530 times, and the highest citation is over 75 times for a single paper.h index is 14. To date, he has applied 6 patents and attended the domestic and international conferences more than 30 times.

Preface

Metal oxide nanomaterials, due to their unique combination of redox chemistry, optical, electrical and semiconductor properties, have played a key role in the successful implementation of gas sensor technology in recent years. The contents of this book present a collection and survey of recent developments in the implementation of metal oxide nanomaterial research methodologies for the discovery and optimization of new gas sensor materials and methods. The book should be of interest to a diverse and broad readership belonging to both academia and industrial research units as it provides a detailed description and analysis of ① basic theory of metal oxide nanomaterials, ② fabrication techniques of metal oxide nanomaterials, ③ characterization techniques of metal oxide nanomaterials, ④ SnO_2- and WO_3- based nanomaterial gas sensors, and ⑤ future of metal oxide nanomaterial gas sensors.

Chapter 1 aims to introduce the fundamental knowledge on gas sensors, including the survey and classification of gas sensors, and the application and perspective of metal oxide nanomaterial gas sensors.

Chapter 2 describes the basic theory of metal oxide semiconductor gas sensors, such as gas sensing mechanism, reaction between gases and metal oxide semiconductor, effect of noble metal doping. Especially, the microstructure model of metal oxide sputtered films and growth mechanisms of metal oxide nanowires are introduced for reference.

Chapter 3 gives a brief review on the fabrication techniques of metal oxide nanomaterials, such as physical vapour deposition, chemical vapour deposition, sol-gel, spray pyrolysis, screen printing, drop coating. In addition, the advantages and disadvantages of each fabrication technique for the production of metal oxide nanomaterials are discussed.

Chapter 4 presents brief review on the characterization techniques of metal oxide nanomaterials. These primary characterization techniques are X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), scanning probe microscopy (SPM), and so on.

Chapter 5 provides the synthesis and characterization of SnO_2-based nanomaterials with various morphologies. Three kinds of SnO_2 nanomaterials, namely SnO_2 thin films, SnO_2 nanowires, and SnO_2 nanorods, are discussed with respect to preparation, microstructure, and gas sensing properties as the potential sensing materials.

Chapter 6 describes the synthesis and characterization of WO_3-based nanomaterials with various morphologies. Three kinds of WO_3 nanomaterials, namely WO_3 thin films, WO_3 nanowires, and WO_3 nanoparticles, are discussed with respect to preparation, microstructure, and gas sensing properties as the potential sensing materials.

Chapter 7 contributes to make brief perspectives on the future development of metal oxide nanomaterial gas sensors.

This book has been finished under fine cooperation of Yanbai Shen (Associate Professor at Northeastern University) and Dan Meng (lecturer at Shengyang University of Chemical Technology). Yanbai Shen completed Chapter 2, 3, 4, 5, 7 and one part of Chapter 6. Dan Meng mainly finished Chapter 1 and other part of chapter 6.

During the writing of this book, I would like to give special thanks to Prof. Dezhou Wei, Dr. Shuling Gao, Dr. Wengang Liu, Dr. Cong Han, Dr. Baoyu Cui, and Dr. Xiaoguang San for their discussion and support. Several students have been involved in collecting relative references and reviewing chapters of this book, and to them my special thanks: Jiawei Ma, Baoqing Zhang, Xianmin Cao, Anfeng Fan. Finally, this book would not have been possible without the financial support of Northeastern University. Many leaders and teachers at College of Resources and Civil Engineering and Institute of Mineral Processing Engineering give me a big support and help. Many thanks to all.

In conclusion, it is hoped that this book can provide extensive understanding and a start point on metal oxide nanomaterial gas sensors for relative operators, researchers, and students. Considering metal oxide nanomaterial gas sensors are complicated, some errors and insufficient or disputed contents do exist in this work. It is deeply appreciated that the readers point out them and make full discussions with the authors.

Authors

01/05/2014

Table of Contents

Chapter 1 Metal Oxide Nanomaterial Gas Sensors: Introduction and Applications

Chapter 2 Basic Theory of Metal Oxide Semiconductor Gas Sensors

Chapter 3 Fabrication Techniques of Metal Oxide Nanomaterials

Chapter 4 Characterization Techniques of Metal Oxide Nanomaterials

Chapter 5 SnO$_2$-based Nanomaterial Gas Sensors

Chapter 6 WO_3-based Nanomaterial Gas sensors

Chapter 7 Future of Metal Oxide Nanomaterial Gas Sensors

Chapter 1 Metal Oxide Nanomaterial Gas Sensors: Introduction and Applications

Detection of chemical species such as industrial toxic and inflammable gases, chemical warfare agents, disease related chemicals, is of very importance to public safety and health. Thus, it is necessary to develop highly sensitive, selective, and stable gas sensors with rapid response and recovery times. Up to now, various kinds of gas sensors based on different detection technologies and mechanisms have been developed. This chapter provides the survey and classification of gas sensors, and the application and perspective of metal oxide nanomaterial gas sensors.

1.1 Survey of Gas Sensors

Gas sensors are commonly used for measuring and indicating the concentration of certain gases in air *via* different detection technologies[1-3]. Typically employed to prevent toxic exposure and fire, gas sensors are often battery-operated devices used for safety purposes. They are manufactured as portable or stationary units and work by signifying high levels of gases through a series of audible or visible indicators, such as alarms, lights, and a combination of signals. While many of the older, standard gas sensors were originally fabricated to detect one gas, modern multifunctional or multi-gas devices are capable of detecting several gases at the same time. Some gas sensors may be utilized as individual units to monitor small workspace areas, or units can be combined or linked together to create a protection system[4,5].

The development of gas sensors has been the subject of intense academic and industrial research activities for the past 50 years. The increasing need to protect the environment and for more efficient control of industrial processes has stimulated the development of various types of gas sensors. These utilize thick or thin films of metal oxides for the detection of inflammable and toxic gases, solid electrolytes for oxygen sensing and to monitor vehicle emissions and production processes, ceramic materials and organic polymers for humidity detection, and artificial olfactory systems with a wide range of applications for the food industry, and these gas sensors are also utilized for medical diagnosis[6,7]. Another rapidly growing application area is the use of metal oxide based sensors for monitoring air pollutants, such as carbon monoxide (CO), nitrogen dioxide (NO_2), and ozone (O_3).

The first thick-film tin oxide gas sensors were constructed by Taguchi at the beginning of the 1960s[8] and various types were subsequently marketed commercially. In the following years, research was carried out to improve the performance of these gas sensors whose operating principle is based on measuring the variation of the electrical resistance of metal oxide semiconductors due to the adsorption of gas molecules on its surface. The materials used in fabrication include zinc oxide (ZnO) for the detection of hydrogen, alcohol, carbon monoxide, and various hydrocarbons; tin oxide (SnO_2) for the detection of inflammable and oxidizing or reducing toxic gases; tungsten oxide (WO_3) for the detection of hydrogen, hydrazine, ammonia, and hydrogen sulfide; titanium oxide (TiO_2) for the detection of oxygen, and so on. Polycrystalline tin oxide is the material most commonly used in commercial gas sensor applications because it is stable enough to allow reproducible measurements[7].

Whether for thick-film or thin-film gas sensors, the response has generally been optimized empirically, without systematic studies of the parameters that influence performance. Various techniques have been used for the deposition of the gas-sensitive layer. These techniques include ultrahigh vacuum and reactive electron beam evaporation[9-16], chemical vapour deposition (CVD) by thermal, plasma or laser technique[17-19], reactive radio-frequency (RF) or magnetron sputtering[20-32], laser ablation[33-38], sol-gel technique[39-42], screen printing technology[43,44], electrochemical deposition[13,45], and pyrosol methods[46-49], etc. Various noble metals, such as platinum, palladium, and silver, which due to their catalytic properties improve the sensitivity and selectivity, may in addition be incorporated into the active layer[50,51].

The improvements in the response of gas sensors depend on developing a better understanding of the principles governing their operation and, in particular, the influence of the microstructure and morphology of semiconductor metal oxide layer on the adsorption mechanism of gas molecules[7]. The requirement to detect simultaneously the component gases contributing to air pollution has stimulated the integration of multiple sensors in single devices, as well as attempts to improve stability and selectivity. The use of nanocrystalline materials allows further improvement in performance compared with conventional polycrystalline materials[52]. Reduction of the grain diameter to values comparable to the Debye length and the extremely high surface-to-volume ratios of the nanocrystalline structure significantly enhance the sensor response.

Nanocrystalline materials are commonly defined as having a mean grain size of less than 100 nm. More generally, nanostructured materials are those, such as a thin film, wire, rod, fiber, or a particle, with at least one dimension below 100 nm or containing atomic domains less than this diameter. Although conventional polycrystalline materials are characterized by grains with dimensions of the order of micrometers containing millions of atoms, a grain of a nanocrystalline material typically contains only a few thousand atoms. Because the surface-to-volume ratio increases rapidly with decreasing the diameter, a reduction in grain size results in an increase in the density of grain boundaries and triple points and thus an increase in the fraction of atoms lying in interfaces compared to those at regular lattice positions. For example, in a polycrystalline material with a grain size of approximately 100 nm, only a small percentage of atoms are in grain boundaries, whereas if the grain diameter is reduced to 5 nm, the small percentage of atoms adjacent to grain boundaries becomes similar to that within the grain interior[53]. Such drastic reduction of grain size causes the changes in the physical and chemical properties, such as electrical and electronic, thermodynamic and mechanical behaviors[54,55].

The gas sensing mechanism is based on the interaction of gas molecules in air with the surface grains of metal oxide layer. The size and interface structure of the grains influence the sensitivity of gas sensor. Detection occurs as a result of complex physical and chemical interactions of the gas molecules with ionized oxygen species adsorbed at the surface of metal oxide grains. The use of a nanocrystalline material increases the detection efficiency because of the greater specific surface area available to interact with the gas molecules and the higher density of grain boundaries that provide a network of diffusion paths into the interior of the material.

1.2 Classification of Gas Sensors[56]

To give a clear introduction of sensing principles, this book classifies gas sensing technologies into two groups: methods based on variation of electrical properties and other properties, as shown in Fig. 1-1.

- Gas sensing methods
  - Methods based on electrical variation with different materials
    - Metal oxide semiconductor
    - Polymer
    - Carbon nanotubes
    - Moisture absorbing material
  - Methods based on other kinds of variation with different methods
    - Optic methods
    - Acoustic methods
    - Gas chromatograph
    - Calorimetric methods

Fig. 1-1 Classification of gas sensing methods

1.2.1 Methods Based on Electrical Variation with Different Materials

1.2.1.1 Metal Oxide Semiconductor

The most common gas sensing materials are metal oxide semiconductors, which provide sensors with several advantages, such as low cost, high sensitivity, and so on. Generally, metal oxides can be classified into two types: non-transition and transition. The former (e.g., Al_2O_3) contains elements with only one oxidation state since much more energy is required to form other oxidation states, while the latter (e.g., Fe_2O_3) contains more oxidation states[57]. Therefore, transition-metal oxides could form various oxidation states on the surface, which is utilized by metal oxide semiconductors as gas sensing materials, compared to the non-transition ones. More precisely, transition-metal oxides with

d^0 and d^{10} electronic configurations could be used in gas sensing applications[58]. The d^0 configuration could be found in transition metal oxides (e. g., TiO_2, V_2O_5, WO_3), and d^{10} appears in post-transition-metal oxides (e. g., SnO_2 and ZnO). Although most common metal oxide semiconductors sensitive to gas concentration are n-type semiconductors, there are also a few kinds of p-type semiconductors like NiO_x (usually doped with n-type semiconductor like TiO_2) that could be used as gas sensing materials. It is shown that 10 wt% NiO_x content is needed to convert n-type conductivity into p-type. The main different between n-type and p-type NiO_x doped TiO_2 film is that as temperature increases, the sensitivity of n-type towards reducing gases is increased, while that of the p-type is decreased[59]. Therefore, p-type semiconductors have relatively lower operating temperatures than n-type ones.

Gas sensors based on metal oxide semiconductors are mainly applied to detect target gases through redox reactions between the target gases and oxide surface[60]. This process usually includes two steps[57]: ① redox reactions, during which O^- distributed on the surface of the materials would react with molecules of target gases, leading to an electronic variation of the oxide surface; and then ② this variation is transduced into an electrical resistance variation of the sensors. The resistance variation could be detected by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy[58].

Metal oxides, such as SnO_2, CuO, Cr_2O_3, V_2O_5, WO_3 and TiO_2, can be utilized to detect combustible, reducing, or oxidizing gases with gas sensors which are mainly based on the resistance change responses to the target gases[61]. SnO_2 is the commonly used gas sensing material. It is an n-type granular material whose electrical conductivity is dependent on the density of pre-adsorbed oxygen ions on its surface. The resistance of SnO_2 changes according to the variation of gas concentration (e. g., liquefied petroleum gas (LPG), methane (CH_4), carbon monoxide (CO) and other reducing gases[62,63]), while the relationship between the resistance and target gas concentration is nonlinear[64]. Other metal oxide semiconductors (e. g., WO_3) are also widely used for gas sensing application. Anodic WO_3 applying electrochemical etching of tungsten shows excellent responses towards hydrogen (H_2) and nitrogen oxide (NO_x)[65]. However, the response of pure WO_3 to NH_3 is rather poor, and because of the interference from NO_x, the selectivity of WO_3 sensors to NH_3 is low. In order to implement WO_3 in gas sensing,

WO_3 should be decorated with copper and vanadium as catalytic additives to improve the response, and the abnormal behavior of sensors should be eliminated[66]. Others like TiO_2 are also used as the sensitive layers for their sensitivity in terms of dielectric permittivity to gas adsorption[67].

Several influence factors, such as the characteristics and structure of the sensing layer, affect the redox reactions and thus decide the sensitivity of metal oxides as gas sensing materials. Among all gas sensors based on metal oxide semiconductors, the sensitivity of SnO_2-based ones is relatively high, leading to its greater popularity. However, this high sensitivity is mainly based on the high working temperature, which is often realized through a heated filament. For most metal oxide gas sensors, the high operating temperature is due to the reaction temperature of O^-[58]. The sensitive layer has to be preheated to an elevated temperature in order to increase the probability of gas molecule adsorption on the layer surface which would consume ions of the sensing materials. As the ions are consumed, the conductivity of the film will increase to realize the sensing function. Besides the heated filament, the micro-hotplate is another choice for keeping the sensing materials at an elevated temperature[68]. Apart from the heating methods, there are also other methods like pre-concentration technology that could be applied to improve the sensitivity of gas sensors[69]. For the methods changing materials' characteristics, the use of composite materials such as SnO_2-ZnO or Fe_2O_3-ZnO is also a good choice for improving the sensitivity of metal oxide gas sensors since they suggest a synergistic effect between the two components[58]. In this method, the sensitivity could be moderated by changing the proportions of each material in the composite.

Gas sensors based on metal oxide semiconductors have been widely utilized. However, for some sensors, their demand of high operating temperature requires more cost and complicated configurations compared to others working at room temperature, which restricts their development and application. To solve this problem, researchers have come up with some methods such as the utilization of micro-sized sensor elements with micro-heaters fabricated by silicon IC technology and temperature pulse operating mode with short heat intervals which facilitates the operation of sensors with minimum power consumption[70,71]. Another problem is the long recovery period needed after each gas exposure, which is not practical for some sensing devices like e-noses, and severely restricts their usage in applications where the gas concentrations may change rapidly. The structural instability and defects of other indicators also limit their application field. In conclusion, faced with inherent challenges from their own nature and other kinds of gas sensors, research on gas sensors based on metal oxide semiconductors should find out some new solutions to overcome their defects. Studies about metal oxide nanomaterials have shown that nanostructured materials could improve the sensitivity and response time of gas sensors[72].

1. 2. 1. 2 Polymers

Generally, gas sensors based on metal oxide semiconductors exhibit significantly greater sensitivity to inorganic gases like ammonia and a few kinds of volatile organic compounds (VOCs) like alcohol (C_2H_5OH) and formaldehyde. However, some other VOCs which could cause adverse health effects when their concentration over a certain threshold cannot be detected by metal oxide semiconductor gas sensors. These VOCs could easily be breathed by humans since they are commonly used as ingredients in household products or in industrial processes where they normally get vaporized at room temperature. Therefore, it is important to monitor the concentration of these vapours to safeguard the health of residents and workers, and also to keep atmospheric emissions under control in order to avoid environmental hazards. Such exact requirements need gas sensing materials like polymers.

Although several studies consider polymer-based gas sensing materials applied in detecting inorganic gases like CO_2 and H_2O[73], they are most frequently used to detect a wide range of VOCs or solvent vapours in the gas phase, such as alcohols, aromatic compounds or halogenated compounds. Like metal oxide semiconductors, when the polymer layers are exposed to the vapour of an analyte, the physical properties of the polymer layer, such as its mass and dielectric properties, will change upon gas absorption. Specifically, the various physisorption mechanisms by which VOCs interact with polymers include induced dipole/induced dipole interactions (also named London dispersion), dipole/induced dipole interactions, dipole/dipole interactions and hydrogen bonds (Lewis acidity/basicity-concept)[74]. In addition to the fact that mechanisms of these property changes are different from those of metal oxide semiconductors, the detection process can be expected to occur at room temperature. According to the different changes in physical properties, polymers used for gas sensing can be further classified into two groups: ① conducting polymers, and ② non-conducting polymers.