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化学传感器：传感材料基础

第1册
化学传感器基本原理及其材料

CHEMICAL SENSORS: FUNDAMENTALS OF SENSING MATERIALS

Basic Principles and Materials of Chemical Sensors

Ghenadii Korotcenkov 主编

影印版

McGraw Hill Education

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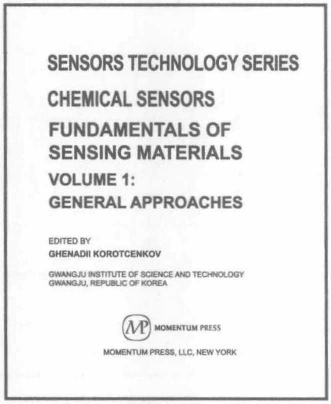
SENSORS TECHNOLOGY SERIES

CHEMICAL SENSORS

FUNDAMENTALS OF SENSING MATERIALS

VOLUME 1: GENERAL APPROACHES

EDITED BY

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Preface to Chemical Sensors: Fundamentals of Sensing Materials

Sensing materials play a key role in the successful implementation of chemical and biological sensors. The multidimensional nature of the interactions between function and composition, preparation method, and end-use conditions of sensing materials often makes their rational design for real-world applications very challenging.

The world of sensing materials is very broad. Practically all well-known materials could be used for the elaboration of chemical sensors. Therefore, in this series we have tried to include the widest possible number of materials for these purposes and to evaluate their real advantages and shortcomings. Our main idea was to create a really useful "encyclopedia" or handbook of chemical sensing materials, which could combine in compact editions the basic principles of chemical sensing, the main properties of sensing materials, the particulars of their synthesis and deposition, and their present or potential applications in chemical sensors. Thus, most of the materials used in chemical sensors are considered in the various chapters of these volumes.

It is necessary to note that, notwithstanding the wide interest and use of chemical sensors, at the time the idea to develop these volumes was conceived, there was no recent comprehensive review or any general summing up of the fundamentals of sensing materials The majority of books published in the field of chemical sensors were dedicated mainly to analysis of particular types of devices. This three-volume review series is therefore timely.

This series, *Chemical Sensors: Fundamentals of Sensing Materials,* offers the most recent advances in all key aspects of development and applications of various materials for design of chemical sensors. Regarding the division of this series into three parts, our choice was to devote the first volume to the fundamentals of chemical sensing materials and processes and to devote the second and third volumes to properties and applications of individual types of sensing materials. This explains why, in *Volume 1: General Approaches,* we provide a brief description of chemical sensors, and then detailed discussion of desired properties for sensing materials, followed by chapters devoted to methods of synthesis, deposition, and modification of sensing materials. The first volume also provides general background information about processes that participate in chemical sensing. Thus the aim of this volume, although not exhaustive, is to provide basic knowledge about sensing materials, technologies used for their preparation, and then a general overview of their application in the development chemical sensors.

Considering the importance of nanostructured materials for further development of chemical sensors, we have selected and collected information about those materials in *Volume 2: Nanostructured Materials.* In this volume, materials such as one-dimension metal oxide nanostructures, carbon nanotubes, fullerenes, metal nanoparticles, and nanoclusters are considered. Nanocomposites, porous semiconductors, ordered mesoporous materials, and zeolites also are among materials of this type.

Volume 3: Polymers and Other Materials, is a compilation of review chapters detailing applications of chemical sensor materials such as polymers, calixarenes, biological and biomimetric systems, novel semiconductor materials, and ionic conductors. Chemical sensors based on these materials comprise a large part of the chemical sensors market.

Of course, not all materials are covered equally. In many cases, the level of detailed elaboration was determined by their significance and interest shown in that class of materials for chemical sensor design.

While the title of this series suggests that the work is aimed mainly at materials scientists, this is not so. Many of those who should find this book useful will be "chemists," "physicists," or "engineers" who are dealing with chemical sensors, analytical chemistry, metal oxides, polymers, and other materials and devices. In fact, some readers may have only a superficial background in chemistry and physics. These volumes are addressed to the rapidly growing number of active practitioners and those who are interested in starting research in the field of materials for chemical sensors and biosensors, directors of industrial and government research centers, laboratory supervisors and managers, students and lecturers.

We believe that this series will be of interest to readers because of its several innovative aspects. First, it provides a detailed description and analysis of strategies for setting up successful processes for screening sensing materials for chemical sensors. Second, it summarizes the advances and the remaining challenges, and then goes on to suggest opportunities for research on chemical sensors based on polymeric, inorganic, and biological sensing materials. Third, it provides insight into how to improve the efficiency of chemical sensing through optimization of sensing material parameters, including composition, structure, electrophysical, chemical, electronic, and catalytic properties.

We express our gratitude to the contributing authors for their efforts in preparing their chapters. We also express our gratitude to Momentum Press for giving us the opportunity to publish this series. We especially thank Joel Stein at Momentum Press for his patience during the development of this project and for encouraging us during the various stages of preparation.

Ghenadii Korotcenkov

PREFACE TO VOLUME 1: GENERAL APPROACHES

This volume provides an introduction to the fundamentals of sensing materials. We have tried to to provide here the basic knowledge necessary for understanding chemical sensing through a brief description of the principles of chemical sensor operation and consideration of the processes that take place in chemical sensors and that are responsible for observed operating characteristics. In spite of the seeming extreme simplicity of chemical sensor operation and application, understanding the mechanisms involved in the process of chemical sensing is usually not so simple. Chemical sensing as a rule is a multistage and multichannel process, which requires a multidisciplinary approach. Therefore, in this volume we provide a description of the important electronic, electrophysical, and chemical properties, as well as diffusion, adsorption/desorption, and catalytic processes.

To our knowledge, this volume is the first attempt to analyze in detail the interrelationships between properties of sensing materials and operating parameters of chemical sensors. This volume describes the properties of sensing materials by emphasizing the specificities of these materials. We consider analyses that have been performed as bridging the gap between scientists studying properties of materials and researchers using these materials for actual chemical sensor design. We hope that the information included in this volume will help readers to approach soundly the selection of either sensing materials or technology for sensing material synthesis or deposition.

Detailed consideration of various materials properties with respect to their application in chemical sensors provides a clear idea of the complexity and ambiguity involved in selecting an optimal sensor material. Research has demonstrated that there is no universal sensing material, and selection of an optimal material is determined by the type of chemical sensor being designed and the requirements that device will have to meet. This volume also illustrates the complementary nature of functionality in sensing materials; for example, high sensitivity usually conflicts with stability. This richness and complexity in behavior cannot be ignored.

This volume is intended to provide readers with a good understanding of the techniques used for synthesis and deposition of sensing materials. Readers will find descriptions of different techniques such as various methods of film deposition, sol-gel technology, deposition from solutions, colloidal processing, the peculiarities of polymers synthesis, techniques used for depositing coatings on fibers, and so on. Description of various methods of synthesis and deposition, accompanied by detailed analysis of the advantages and shortcomings of those methods, provides the understanding necessary for considered selection of a technology for forming a sensitive layer.

Analysis of metal oxide modification methods highlights the opportunities for control of the properties of sensing materials, and demonstrates that a choice of methods should be based on consideration of all possible consequences of the technical decision that is made.

Combinatorial and high-throughput materials screening approaches analyzed in this volume will be also of interest to researchers working on materials design for chemical sensors.

We are confident that the present volume will be of interest of anyone who works or plans to start activity in the field of chemical sensor design, manufacturing, or application.

Ghenadii Korotcenkov

About the Editor

Ghenadii Korotcenkov received his Ph.D. in Physics and Technology of Semiconductor Materials and Devices in 1976, and his Habilitate Degree (Dr.Sci.) in Physics and Mathematics of Semiconductors and Dielectrics in 1990. For a long time he was a leader of the scientific Gas Sensor Group and manager of various national and international scientific and engineering projects carried out in the Laboratory of Micro- and Optoelectronics, Technical University of Moldova. Currently, he is a research professor at Gwangju Institute of Science and Technology, Gwangju, Republic of Korea.

Specialists from the former Soviet Union know G. Korotcenkov's research results in the study of Schottky barriers, MOS structures, native oxides, and photoreceivers based on Group III–V compounds very well. His current research interests include materials science and surface science, focused on metal oxides and solid-state gas sensor design. He is the author of five books and special publications, nine invited review papers, several book chapters, and more than 180 peer-reviewed articles. He holds 16 patents. He has presented more than 200 reports at national and international conferences. His articles are cited more than 150 times per year. His research activities have been honored by the Award of the Supreme Council of Science and Advanced Technology of the Republic of Moldova (2004), The Prize of the Presidents of Academies of Sciences of Ukraine, Belarus and Moldova (2003), the Senior Research Excellence Award of Technical University of Moldova (2001, 2003, 2005), a Fellowship from the International Research Exchange Board (1998), and the National Youth Prize of the Republic of Moldova (1980), among others.

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CHAPTER 1

Basic Principles of Chemical Sensor Operation

M. Z. Atashbar
S. Krishnamurthy
G. Korotcenkov

1. INTRODUCTION

In recent years increased knowledge has led to significant development of chemical sensors for detection and quantification of chemical species. Chemical sensors have found a wide range of applications in clinical, industrial, environmental, agricultural, and military technologies.

Chemical sensors are characterized by parameters such as sensitivity, selectivity, response and recovery time, and saturation. Chemical sensors can be classified in a number of ways, depending on their principle of operation. In this chapter we describe the fundamental concepts of the following classes of chemical sensors: electrochemical, conductometric, capacitive, work function, chemFET, catalytic, Schottky diode, acoustic wave, mass-sensitive, optical, chemoluminesese, photoacoustic, thermal, surface plasmon resonance, thermoelectric, thermal conductivity–based, flame ionization, and Langmuir-Blodgett sensors.

2. ELECTROCHEMICAL SENSORS

Electrochemical sensors constitute the largest and most developed group of chemical sensors and have taken a leading position with respect to commercialization in the fields of clinical, industrial, environmental, and agricultural analysis (Korotcenkov et al. 2009). Electrochemical sensors are based on the detection of electroactive species involved in chemical recognition processes and make use of charge transfer from a solid or liquid sample to an electrode or vice versa. An electrochemical sensing method essentially requires a closed electrical circuit, which enables the flow of direct or alternating current to make measurements. Figure 1.1 illustrates a basic structure of an electrochemical sensor. For gas sensors, the top of the casing has a membrane which can be permeated by the gas sample.

For current to flow, at least two electrodes are needed. One electrode is an active electrode or working electrode (WE), where the chemical reaction takes place; the other is a return electrode, which is called a counter or auxiliary electrode (AE). A current is created as positive ions flow to the cathode and negative ions flow to the anode. To measure the electrochemical potentials produced by the electrodes and the electrolyte, a third electrode, called a reference electrode (RE), can be used. The reference electrode corrects the error introduced as a result of polarization of the working electrode. The working electrode is often made up of a layer of noble metal or catalytic metal such as platinum-, palladium-, or carbon-coated materials. This working electrode is covered with a hydrophobic membrane that acts as a transport barrier for the target chemical molecules (analyte), allowing the chemical species to diffuse to the working electrode and also preventing leakage of the electrolyte (Zao et al. 1992). To produce a measurable signal, the electrodes must have a large surface area in order to maximize the contact area with the analytes. Electrodes generally have a special coating to improve their rate of reaction and to extend their working life. An electrolytic medium is required to carry the ionic charges. Selective reactions can be accomplished by careful choice of the electrolyte and hence it is the first stage in enhancing selectivity to a particular analyte. The sensor formed by the combination of an electrolyte, electrodes, and an external circuit is called an electrochemical cell. The cell can be configured to extract electrical signals such as current, potential, conductance, or capacitance (Fradeen 2003).

A common application for potentiometric and amperometric sensors is for water analysis. The most common is the pH sensor system. A wide range of gaseous analytes such as oxygen, carbon oxides, nitrogen oxides, sulfur oxides, and combustible gases also can be detected and quantified using electrochemical sensors. Gases such as oxygen, nitrogen oxides, and chlorine, which are electrochemi-

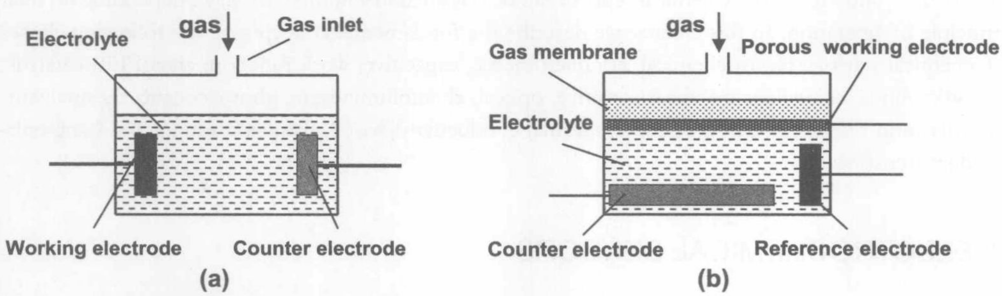

Figure 1.1. Schematic diagram of electrochemical gas sensors with (a) two- and (b) three-electrode configurations. (Reprinted with permission from Korotcenkov et al. 2009. Copyright 2009 American Chemical Society.)