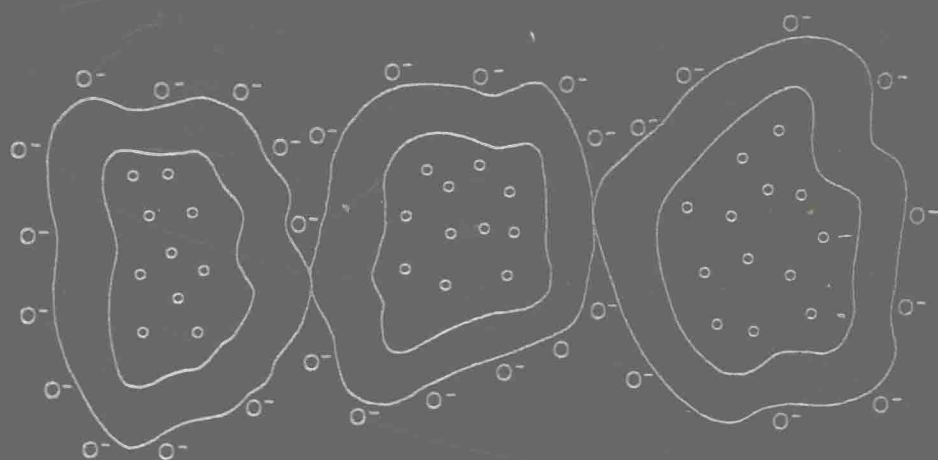

CHEMICAL SENSING

with

SOLID STATE DEVICES



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Chemical Sensing with Solid State Devices

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ACADEMIC PRESS, INC.
Harcourt Brace Jovanovich, Publishers
Boston San Diego New York
Berkeley London Sydney
Tokyo Toronto

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ACADEMIC PRESS, INC.

1250 Sixth Avenue, San Diego, CA 92101

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

24-28 Oval Road, London NW1 7DX

Library of Congress Cataloging-in-Publication Data

Madou, Marc J.

Chemical sensing with solid state devices/Marc J. Madou, S. Roy Morrison.

p. cm.

Bibliography: p.

Includes index.

ISBN 0-12-464965-3

1. Chemical detectors. I. Morrison, S. Roy (Stanley Roy)

II. Title.

TP159.C46M33 1988

660.2'8'00287—dc19

88-12643

CIP

Printed in the United States of America

89 90 91 92 9 8 7 6 5 4 3 2 1

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Preface

Solid-state sensors that measure universal physical parameters such as pressure, position, height, acceleration, temperature and others have been commercially successful. Less success has been attained by solid-state sensors designed to measure important chemical species such as protons (pH), O_2 , CO_2 , H_2S , CO, propane and glucose, to mention a few. There is no doubt, however, that we can look forward to rapidly increasing use of solid-state sensors as the results of current research lead to their improvement and because of the huge cost difference compared with the more complex analytical equipment, such as gas chromatographs. In this book we explore the theoretical background needed to understand solid-state chemical sensors, explore the major developments in the area of chemical sensors over the last two decades, and explore the reasons why these low-cost solid-state sensors have not become more of a commonplace item in our daily lives. We also suggest possible directions for future research and development.

The book is meant to provide guidance through the multidisciplinary world of chemical sensors for scientists of various training, chemists, biologists, engineers and physicists. Researchers of these various backgrounds, working together, are needed to provide the improved sensors of the future. We hope the essentials will also be understandable to students with some training in physics and chemistry and a general knowledge of electronics.

In the first part of the book we present a review of the necessary theoretical background in solid-state physics, chemistry and electronics. We examine the semiconductor and solid electrolyte bulk models as well as the

solid/gas and solid/liquid interface models, because the species to be detected interacts with the surface of the solid. We also discuss the theory of membranes and catalysts, both of which can be very important in almost any type of chemical sensor. We have not attempted to provide a similar fundamental background in biology to support the chapter on biosensors. Other sources must be used if one needs to familiarize oneself with the basics in that field.

In the second part of the book we discuss more complete sensor devices (the essential components are combined) and discuss the latest development in this area. Due to the wide range of types of chemical sensors, we have limited ourselves to those sensors in which a physicochemical interaction between a solid and the species to be detected causes an electrical effect in the solid that can be quantified.

We emphasize three classes of solid sensors: semiconductor sensors, where the species to be detected is adsorbed or absorbed and changes the electronic conductivity of the semiconductor; solid electrolyte devices for use in gas or liquid, where the species to be detected affects the Nernst potential or changes the ionic current through the solid; and ChemFETs, where the species to be detected affects the potential at the gate of a field-effect transistor. New areas such as amperometric microelectrode arrays are discussed as well as the economic aspects of chemical sensors.

We have included numerous references to enable the reader to focus on a particular detection problem. We felt this would be preferable to trying to describe all combinations of sensors and detectable species that could be of interest. This has allowed us to present the background information and the common features in more detail.

Acknowledgments

The authors wish to acknowledge the critical review of parts of the manuscript by Ms. Anuradha Agarwal, Mr. Scott Gaisford, Dr. Jose Joseph, Dr. Mike McKubre, Dr. Ary Saaman, Dr. Kristien Mortelmans, Dr. Takaaki Otagawa, Dr. Peter Kesketh, Dr. Ivor Brodie, Mr. John Mooney, Dr. Karl Frese, Dr. Robert Lamoreux, Mr. Bernard Wood and Dr. Jon McCarty, all from SRI. SRM would like to express his appreciation to Professor G. Heiland for restimulating his interest in this exciting field. MJM would like to acknowledge the moral support by Dr. Ivor Brodie and would like to express his gratitude to SRI for the financial support received.

Both of us would like to thank our wives, Phyllis and Marleen, for their patient support and active participation in the preparation of the book.

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1

Introduction

The chemically sensitive solid-state devices discussed in this book are based on the electrical response of the solid to its chemical environment. That is, we are interested in solids whose electrical properties are affected by the presence of a gas-phase or liquid-phase species; this change in electrical properties is observed and then used to detect the species.

In addition to sensors based on changes in electrical parameters, many other types of solid-state chemical sensors are based on other principles, such as acoustics (e.g., bulk and surface acoustic wave devices (BAW and SAW)), optics (e.g., optical waveguides), and thermochemistry (e.g., microcalorie sensor and microenthalpy sensor (or, in more classical form, catalytic bead sensors)). Of course, more classical techniques, such as gas chromatography, ion mobility spectroscopy and mass spectroscopy, continue to be used for sensing purposes.

The major advantages of solid-state sensors are their simplicity in function, small size and projected low cost. The simplicity in function is in sharp contrast to some of the more classical analysis techniques mentioned in the preceding paragraph, which require complex equipment and skilled operators to run an analysis. The projected cost is low because the size of the solid sample used is small (typically measured in centimeters to micrometers). For some forms of solid-state sensors now under development, the cost is further minimized by the use of batch, planar fabrication technologies in manufacturing the device.

The major disadvantages of most solid-state chemical sensors are lack of stability, lack of reproducibility, and lack of selectivity as well as insufficient sensitivity for certain purposes. These problems, and the research

underway to alleviate them, will be discussed throughout the text. However, in many applications the disadvantages are not prohibitive; hence solid-state sensors are commercially available and in use. Also, through the use of filters, membranes, catalysts and other variations, sensors with different selectivities can be produced. Then arrays of sensors feeding a microcircuit can in principle overcome many of the above disadvantages while still retaining a reasonable cost.¹

The term “solid-state sensors” will be used quite broadly here to include sensors incorporating not only classical semiconductors, solid electrolytes, insulators, metals and catalytic materials but also different types of organic membranes. The term even extends to sensors incorporating liquid membranes that, by judicious use of polymeric supports and gelling agents, appear solid (e.g., polymer-supported ion-selective membranes and sensors incorporating hydrogels).

The most frequently recurring topics discussed in the book are introduced in this chapter.

1.1 Silicon-Based Chemical Sensors

Silicon-based sensors, which are just one type of semiconductor-based solid-state sensor, are quite a recent development. One important class of these sensors arises as variations on field-effect transistors (FETs). In a FET one has a thin channel of conductance at the surface of the silicon, which is controlled by the voltage applied to a metal film (a *gate*) separated from the channel of conductance by a thin insulator layer (e.g., silicon dioxide). It was found that if the metal film was removed from the FET and either adsorbed gases or ions from the ambient atmosphere or else liquid appeared at the surface of the gate dielectric, the effect was similar to applying a voltage at the gate.²

Thus, great interest was generated regarding the possibility of using well-understood integrated circuit (IC) technology to produce amplifying devices (such as the FET) that would respond to molecules and ions in solution or gases. Selectivity can be induced in these sensors by the appropriate incorporation of, for example, certain pH-sensitive insulators and ion-selective membranes in ion-sensitive field-effect transistors (ISFETs), enzymes in enzyme-sensitive field-effect transistors (EnFETs), antibodies or antigens in immuno-FETs (ImmFETs), whole tissue layers in BioFETs and certain bilayer lipid membranes (BLM) in BLMFETs. Often

the broader term “ChemFET” is used to describe a chemically sensitive FET. ChemFETs are discussed in Chapters 8 and 9. In particular, it has been projected that this new class of chemically sensitive electronic devices will at least have some of the following attractive sensor attributes:

- Small, rugged, low-cost, batch-fabricated, solid-state structures, possibly disposable.
- Arrays of sensor elements for multispecies detection incorporating redundancy (in case one element breaks, or for averaging) and electronics on the silicon chip to provide low-impedance output, filtering, multiplexing, and so on, or, in other words, an integrated monolithic (e.g., all-silicon) sensor.
- Arrays of sensor elements also incorporating on-chip memory: both a read-only memory (ROM) to unravel complex responses, such as nonlinearities, or to offset predictable drift patterns, and a random-access memory (RAM) to let the user interact with the sensor to set it up for a specific application. In other words, one could visualize a “smart” sensor.

The first desirable feature can be achieved with many solid-state sensors. The second and third features are, in monolithic form, only possible when semiconductor materials such as Si and GaAs are used. To some degree, the same features are also possible for many types of hybrid sensors—that is, sensors in which electronic functions are on a separate semiconductor chip close to the chemical sensing function; the sensor and the chip are affixed to a common substrate and connected with short conductor lines (signal lines).

The development of FET-based chemical sensors, which seemed very promising in the early 1970s, is plagued by a tremendous number of technological and fundamental problems. These problems are reflected in the rather large irreproducibility of performance and important drifts and degradation with time, which frequently even precludes the use of disposable devices.³ The high investment costs have also postponed development.

The technological problems are mostly associated with attempts to integrate closely chemical-sensitive layers and electronics on the same chip: for example, electrolyte leakages leading to shunting of the amplifier, light sensitivity of the FET gate, incompatibility between Si technology and the many types of gate materials needed to induce chemical sensitivity and selectivity, and encapsulation in general. For *in vivo* use of sensors biocompatibility has proven to be the most difficult hurdle to overcome. Many

alternative FET-based approaches have been proposed since the initial studies, a few of which could possibly circumvent some of the former technological problems. These alternative Si-based devices, which include the ion-controlled diode (ICD), the extended-gate field-effect transistor (EGFET), the electrostatically protected field-effect transistor and others, will be discussed in detail in Chapter 9. Biocompatibility of microsensors is often more of a black art than an exact science and no satisfying solutions are available today. We briefly touch upon the subject in Chapter 7.

A fundamental problem with most FET-based devices used in liquids, which causes drift and irreproducibility, is associated with the inability to establish a well-defined reference potential on either side of the chemically sensitive membrane. In ChemFETs, where the gate potential is to be affected by the concentration on the other side of the membrane, the membrane is placed directly on top of an insulating gate. With this configuration, the device lacks the internal reference electrode and electrolyte needed for the establishment of a stable internal reference potential. Literature describing the problem of no internal reference electrode is limited. However, in coated wire electrodes (CWEs), where membranes are put directly on a metal wire, also without the provision of an internal reference electrode or internal electrolyte, stability problems similar to those encountered with ChemFETs were observed. In the CWE field a much more thorough study was made of this phenomenon. Because this work is of considerable importance to future developments in the field of FET-based Si sensors, we reviewed it in detail in Section 6.3.

An external reference electrode (to be used effectively to provide a constant ground potential) is also hard to make in the desired form (planar and micro). A true external reference electrode (see Section 6.1) includes an electrode of the second kind, such as the Ag/AgCl system in contact with a reservoir of the potential-determining ions (e.g., 0.1 M of Cl^- for a Ag/AgCl electrode), and a device (e.g., a glass frit) to restrict mixing of the analyte (the solution to be analyzed) with the internal electrolyte. These features are very hard to fabricate on a microscale. Consequently, so-called pseudo reference electrodes are often used instead. In these electrodes the Ag/AgCl is directly exposed to the analyte rather than to a small reservoir of reference electrolyte. With this compromise the potential of the external reference electrode in a FET device is then only fixed when the concentration of potential-determining ion for the reference system (e.g., Cl^- for a Ag/AgCl electrode) is constant in the analyte.

Another fundamental problem with certain FET devices (e.g., the ImmFET (see Chapter 9)) has been the failure to find a perfectly polariz-