Chemical Sensor Technology

Vol. 1

Edited by
Tetsuro SEIYAMA
Professor Emeritus, Kyushu University, Fukuoka, Japan

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Foreword

The importance of chemical sensors has been recognized generally and active efforts are now being stimulated toward basic research and practical application of chemical sensors. As is well known, chemical sensors have already been applied successfully in various fields and they have without a doubt become key requisites in modern high-technological society. Needless to say, while the expectations of society with regard to chemical sensors are great, in reality chemical sensors have not yet met all these expectations. Further progress in basic research and applied technology on chemical sensors are thus eagerly awaited.

Currently, innovative research and development looking toward the 21st century is being conducted on functional materials such as high temperature superconductors and in the fields of microelectronics including optoelectronics, biotechnology, and so on. It is hoped that together with progress in these areas many great innovations in the field of chemical sensors will also be made.

This new series of annual reviews, *Chemical Sensor Technology*, aims at contributing to the progress of research and development of chemical sensors. The editorial board will try to include in the volumes as many innovative studies on chemical sensors as possible. Contribution of articles to the series will be sought worldwide from investigators and engineers working in the field. The board humbly requests the support and cooperation of chemical sensor researchers everywhere for this new series.

The Editorial Board

Preface

Chemical sensors continue to grow rapidly in importance encompassing a broad spectrum of technologies covering safety, pollution, fuel economy, medical engineering and industrial processes. Various types of chemical sensors have been devised for detection and monitoring of chemical substances in gases, solutions and organisms. Much work is being done to produce sensitive, selective, reliable and inexpensive sensors.

The International Meeting on Chemical Sensors held in Fukuoka in 1983 drew more than 400 interested participants from 22 countries. This was followed by the Second International Meeting in Bordeaux in 1986. The Third Meeting is scheduled to be held in Toronto in 1989. The proceedings of these meetings, published in English, were very well received worldwide, stimulating further interest and research in the field.

As a result it has been decided to publish a series of annual reviews entitled *Chemical Sensor Technology*. I wish to express my sincere gratitude for the enthusiasm of many famous investigators regarding this project and for their participation in the Editorial Board. This is the first volume of the series and the preparation of the second volume is currently under way. This as well as future volumes will report the latest progress being made in research and technology, both basic and applied, regarding chemical sensors.

Contributors, selected by an international editorial board, are encouraged to describe not only the academic or technological essence of a given subject but also the background and philosophy of the subject, evaluation of achievements and future problems. The series as a whole will cover research and development of chemical sensor devices, their applications, sensor materials and other related subjects.

It is hoped that this series of publication will be useful to many investigators and engineers working in the field of chemical sensors.

April, 1988

Tetsuro SEIYAMA
Editor

Contents

Chemical Sensors
—Current State and Future Outlook

TETSURO SEIYAMA
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1. INTRODUTION

1.1 Short History of Chemical Sensors

The history of the development of chemical sensors is summarized in Table 1. About 30 years have passed since the appearance of chemical sensors. The devices, which in the beginning were called by a variety of names, gradually, came to be known by the single term, "sensor," and the classification of sensors into physical and chemical types has been established. Over the past 30 years, the chemical sensor has made great advances and has taken root in human life and industry as a feature of modern technology. Moreover, remarkable progress is expected in the future. Numerous chemical sensors of various types were proposed in the early 1960s. Then in the 1970s, new sensing devices, ion-sensitive field effect transistors (ISFET) and Pd-gate FET, were proposed, and at the same time some of the sensors proposed earlier began to be produced commercially. This period may be considered the first stage of chemical sensors, which culminated in the first International Meeting on Chemical Sensor held in Fukuoka in 1983. As seen from the table, many new types of sensors were proposed during this first stage, with some of them proceeding on to production, and the period can be said to be an impressive and hopeful opening stage. The second stage should see even more advances as a result of investigations and studies which are developing in their various ways and forming their various territories. Success in this stage requires the effective combination of basic research, high technology and strong effort.

1.2 General Forecast of Future Technology

Generally speaking, the innovative and remarkable progress made from the 1940s through the 1960s cannot be expected in the 1980s, but improvement, combination, and systematization of the present technology can. Electronics, including optoelectronics and so-called "mechatronics" are playing the leading role in the development of sensor technology in the eighties. New basic technologies are expected to appear in the

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1990s, based on the life sciences (e.g, biotechnology) and on new materials science. Expected developments in chemical sensors are described below.

TABLE 1 History of the Development of Chemical Sensors

1923	Catalytic combustion-type sensor	Jonson
1930	Practical use of glass electrode for pH measurement	MacInnes
1938	Humidity sensor using LiCl Film	Dunmore
1952	Galvanic cell-type gas sensor	Hersch
1957	Theory of the electromotive force of a solid electrolyte cell	Wagner
1961	Solid electrolyte-type sensor	Weissburt & Ruka
1961	Ion electrode sensor	Pungor
1962	Biosensors-basic concept	Clark
1962	Oxide semiconductor-type gas sensor	Seiyama
1962		Taguchi
1964	Piezoelectric quartz crystal sensor	King
1964	Practical use of thermister-type gas sensor (Shigenshishiki)	Denshisokki Co.
1965	Practical use of catalytic combustion-type sensor	Riken-Keiki Co.
1966	Glucose sensor	Updike & Hicks
1967	Practical use of oxide semiconductor-type gas sensor	Figaro Eng. Inc.
1967	Practical use of ion electrode sensor	Metrimpex Co.
1970	ISFET	Bergfeld
1970	Optical fiber gas sensor	Harsick
1974	Practical use of electrochemical gas sensor (Potentiostatic electrolysis type)	Belanger
1975	Pd gate FET hydrogen sensor	Lundtröm
1976	Practical use of oxygen sensors for automobiles	Bosch Co.
1976	Practical use of the $MgCr_2O_4$-TiO_2 system humidity sensor	Matsushita Elec. Ind. Co.
1976	Practical use of the Pd gate FET sensor	Lundström
1977	Enzyme FET	Janata
1982	Solid state gas sensor symposium (Badhonef)	
1983	First International Meeting on Chemical Sensors (Fukuoka)	
1985	Practical use of ISFET	Kuraray Co.
1986	Second International Meeting on Chemical Sensors (Bordeaux)	

2. CURRENT STATE OF CHEMICAL SENSORS AND ADVANCES EXPECTED IN THE NEAR FUTURE

As noted above, advances in chemical sensors in the near future will probably follow the course of improvement, combination and systematization. Regarding the improvement of chemical sensors, much is epected by way of excellent sensing materials and advanced microfabrication for miniaturization and energy saving purposes. As for combination, a high performance sensor integrating several devices will be developed. A high performance sensor fabricated by integrating sensing devices with various sensing characteristics and micro-computer should enhance the accuracy and selectivity of gas detection. A serious defect in current sensor systems, *i.e.* false alarms or failure to alert, could be avoided through a double or triple checking system by integrated combination and result in a fool proof sensor. The attached microprocessor will further advance systematization. Automatic control of machines or insturments of monitoring systems, alarm systems and other control systems would advance security, amenities, and convenience of home appliances in daily life as well as process control in industry. These automatic control systems may be regarded as important aspects in the development of "mechatronics".

As described above, chemical sensors have shown broad advances and various types of chemical sensors have been commercialized. In the future unless a newly proposed sensor system indicates clear superiority or merit compared with current systems, it stands very little chance of being developed for practical use.

2.1 Improvements in Sensing Materials

The general procedure for research on chemical sensors is summarized in Fig. 1.

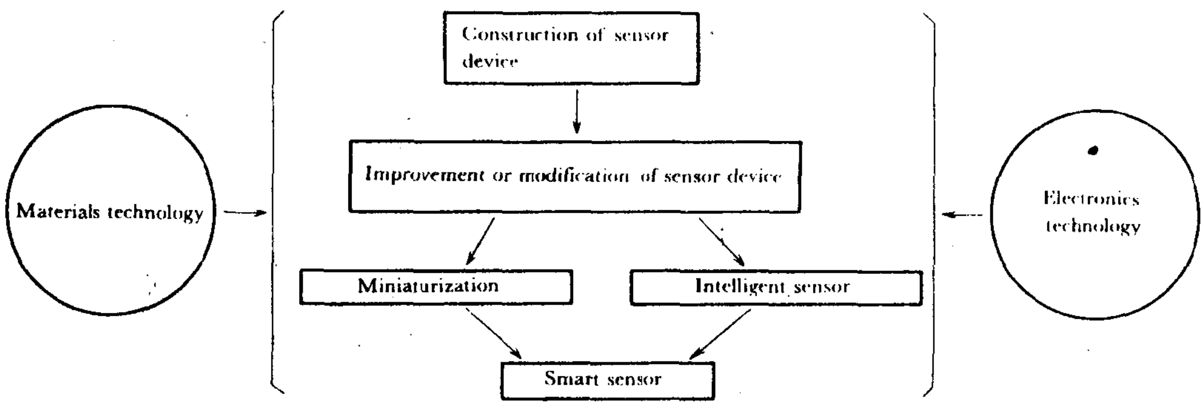

Fig. 1 Research and development on chemical sensors.

As shown in this figure, research on materials and technology of electronics interface are indispensable to the development of chemical sensors. Both must be intimately combined in every process in order to produce a superior sensor system. Relatively recent and interesting sensor materials, excluding those for bio-sensors, are summarized in Table 2. Many new materials and their processing technology have been reported. For the advancement of sensor research, it is important to establish a guiding concept concerning the construction of the sensor device and achieve an exact understanding of the sensing mechanism. Otherwise, results obtained by haphazard experiments may prove to be less useful in the development of chemical sensors.

The trend of studies on materials in Table 2 can be classified into five categories as follows :

1) Use of mixed oxides such as perovskite-type oxide for semiconductor-type gas sensors.

2) Use of auxiliary additiv phase for the solid electrolyte-type chemical sensors (extension of sensing ability to in lude various gaseous species).

3) Design of sensing mat ials based on pore structure for humidity sensors.

4) Use of L. B. film for he miniaturization of various types of sensors and use of organic silicone compoun s or glass as the support for sensing materials or as encapsulation materials.

5) Others regarding new type of sensing or sensors.

TABLE 2 Materials Used as Chemical Sensor Elements

Sensor materials	Sensing gas	Remarks	References†
$Sr_{1-x}Ca_xFeO_{3-x}$	CH_4	Semiconductor type	1-38
$Au/\alpha\text{-}Fe_2O_3\text{-}TiO_2$	CO	Semiconductor type	1-18
$Zn_xGeO_yN_z$	NH_3	Semiconductor type (Oxynitride of Zn and Ge)	1-07
$SrTi_{1-x}Al_xO_{3-x}/Cr_2O_3$	O_2	Semiconductor type (Lean Burn)	1-08
$Pt\text{-}SrTi_{1-x}Mg_xO_{3-\delta}$	O_2	Semiconductor type	1-09
Pt-, Ru-Phtalocyanine	NO_2	Organic semiconductor type	1-22
Pd-Phtalocyanine + Pt coil	trichlorethylene	Organic semiconductor type	1-27
Tetraazannulene	NO_x	Organic semiconductor type L. B. film	1-01
ORMOSIL	SO_2, NO_2	Organic silicone recin FET type	4-15
Zeolite	H_2, CH_3OH etc.	FET type	4-14
12-19 anthroyloxy -stearate	NH_3	L. B. film	PL-8
Ag β-Alumina	As_2O_3 (AsH_3)	Solid electrolyte type	2-09, 2-04
$PbSnF_4$, PbF_2, LaF_3	O_2	Solid electrolyte type (low temperature operation)	2-02
$Na_2O\text{-}B_2O_3\text{-}La_2O_3\text{-}TiO_2$	humidity	Porous glass ionic conductor type	3-10
$Au\text{-}TiO_2$	SiH_4	Metal-semiconductor junction type diode	*Sur. Sci.* **146**, 10 (1984)
Zeolite	CO_2	Exothermal heat evolution bridge type	3-10

†References from *Proc. 2nd Int. Meeting on Chem. Sensors*

Use of mixed oxides such as perovskite-type oxide in the semiconductor type sensor has been studied extensively. In Fig. 2, the band gaps of various oxide semiconductors are arranged.[1)] Many mixed oxides can be seen in the figure. Some of the mixed oxides may prove to be excellent and useful sensor materials by improving the donor-acceptor level, surface level, and surface reactivity, which strongly influence the sensing characteristics of this type of sensor.

Oxidation and reduction property of oxides is also important in semiconductor type sensors and solid electrolyte sensors to maintain not only better sensing properties but also long-term stability of the sensor in ambient atmosphere. The oxidation and reduction of metal oxides can be expressed by the following two reactions.

$$H_2 + MO_x \rightleftarrows H_2O + MO_{x-1} \quad (1)$$

$$MO_{x-1} + 1/2O_2 \rightleftarrows MO_x \quad (2)$$

Formation of mixed oxides such as perovskite-type (ABO_3) oxides promote stability in thermal and chemical atmosphere. It is also possible to improve conductivity by adjusting the composition. For instance, in perovskite-type oxides, p- or n-type semiconductor and in some cases oxygen anion conductor can be obtained by the appropriate combination of A and B site metals and by doping a third metal element.

The electronic character of organic semiconductors such as phthalocyanine can