

微纳技术著作丛书（影印版）

CMOS技术中的集成 化学微传感系统

Integrated Chemical Microsensor Systems
in CMOS Technology

A. Hierlemann



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CMOS技术中的集成化学微传感系统

Integrated Chemical Microsensor Systems in CMOS Technology

- Provides a comprehensive treatment of the highly interdisciplinary field of CMOS chemical microsensor systems.
- It is targeted at students, scientists and engineers who are interested in gaining an introduction to the field of chemical sensing since all the necessary fundamental knowledge is included. However, as it provides detailed information on all important issues related to the realization of chemical microsensors in CMOS technology, it also addresses experts well familiar with the field.

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CMOS 技术中的 集成化学微传感系统

**Integrated Chemical Microsensor
Systems in CMOS Technology**

A. Hierlemann

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内 容 简 介

本书涵盖了 CMOS 化学微传感系统的各个领域, 详细论述了化学微传感器在 CMOS 中的集成技术。在做了简要介绍之后, 阐述了所有必备的基础知识, 介绍了各种化学敏感方法, 并介绍了 CMOS 技术及其在微传感器中的应用, 最后对未来的发展作出了展望。

本书内容丰富, 涵盖了大量的基础知识及 CMOS 技术中化学微传感器的相关重要信息, 适合希望从事此领域工作的学生、工程技术人员、科学家阅读, 对于熟悉本领域的专家也很有参考价值。

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序

科学出版社准备出版一套《微纳技术著作丛书》，包括原创作品和引进作品（影印或翻译）两种形式，并聘请专家组成编委会。这是一件大事，希望能坚持把它办好。

微纳米技术作为 21 世纪重要的一项技术，已成为国际科学界和工程技术界研究的热点。近年来，微米纳米技术进展迅速，已经发展成为一个包含机械、材料、电子、光学、化学、生物、基因工程、医学等基础学科的综合领域，而不仅仅属于任何单一的科学和技术门类。就其产品而言，也早已超越了人们广为熟悉的微型加速度传感器和纳米碳管等，呈现出向各个科学和技术领域全面渗透的趋势。

由于微纳米技术使得人们除了可以在同一基片上实现包括机械、流体、化学、生物、光学等器件外，也可以将信号处理和传输系统集成在同一基片上用以处理信息，决定计划，控制周围环境，从而大大提高最终产品的综合性能，实现高度智能化。在未来的航空航天、生物医学、环境监控、无线通信、汽车和交通、石油化工、能源、工农业、国家安全、食品和消费的各个领域都将有广泛应用，对国民经济、科学技术、社会发展与国家安全具有重要意义。今后的几十年里，随着微米纳米技术的迅速发展和向现代科学和技术的各个门类渗透，其对我们现代生活的各个方面带来的影响将是长期和深远的。从某种意义上来说，微米纳米技术的发展，可能改变人类的工作和生活方式，乃至基本概念，其潜在的影响有可能和以计算机技术为代表的微电子工业对世界的影响相提并论。

正是由于其诱人的应用前景和巨大的潜在市场，微米纳米技术目前已成为世界各国大力投资进行研究和发展的热点领域，其研究范围包括了材料、器件和系统，涉及的技术包含机理研究、设计分析、计算仿真、制造工艺、系统集成或组装、测控技术和应用研究等。随着微纳米技术的迅猛发展，近年来国外有大量这方面的专业书籍出版。

《微纳技术著作丛书》涵盖材料开发、系统设计、检测技术、集成技术、通信网络、传感系统、微加工技术等方面，它们都是本领域的研究热点。这套丛书的出版对促进我国微米纳米技术的发展将有很大的推动作用。

这套丛书中，原创作品收录的都是国内从事微纳技术的一线研究人员在本领域的研究成果与心得，具有很强的独立性、创造性和系统性。引进作品都是与国际知名的出版集团合作，经国内专家的甄别，挑选出能反映国外最新研究成果、对国内读者又有借鉴价值的作品，具有权威性、前瞻性和可读性。因为微纳米技

术是一个交叉学科领域，我们有意识的选择了一些由多人合写的专著。通常这类著作都是由相关领域的知名专家，各自在每一章节涵盖一个专题，既有进行综合性的论述，也有个人的具体独创性研究。这样的书籍，通常能帮助读者既获得某一领域的研究概况，又能从一个具体的应用专题中获得收益。

2007年初推出的第一批影印版图书，我和王万军教授进行了评读，此套丛书很实用，不少作者在该领域有很高的声望。我们建议致力于微米纳米技术的研究人员，包括研究生、技术人员，能够花些时间阅读。

总之，我们对科学出版社组织出版这套丛书的举措很赞赏，也希望他们能将这一工作认真、长期地做下去。同时，我们也希望国内的专家能够积极、踊跃地加盟，为我国微米纳米技术的推进做出贡献。

2006年12月7日

Preface

This book provides a comprehensive treatment of the very interdisciplinary field of CMOS technology-based chemical microsensor systems. It is, on the one hand, targeted at scientists and engineers interested in getting first insights in the field of chemical sensing since all necessary fundamental knowledge is included. On the other hand, it also addresses experts in the field since it provides detailed information on all important issues related to realizing chemical microsensors and, specifically, chemical microsensors in CMOS technology. A large number of sensor and integrated-sensor-system implementations illustrate the current state of the art and help to identify the possibilities for future developments. Since microsensors produce “microsignals”, sensor miniaturization without sensor integration is in many cases prone to failure. This book will help to reveal the benefits of using integrated electronics and CMOS-technology for developing chemical microsensor systems and, in particular, the advantages that result from realizing monolithically integrated sensor systems comprising transducers and associated circuitry on a single chip.

After a brief introduction, the fundamentals of chemical sensing are laid out, including a short excursion into the related thermodynamics and kinetics. Fabrication and processing steps that are commonly used in semiconductor industry are then abstracted. These more fundamental sections are followed by a short description of microfabrication techniques and the CMOS substrate and materials. Thereafter, a comprehensive overview of semiconductor-based and CMOS-based transducer structures for chemical sensors is given. The corresponding chemically sensitive materials and the related applications are mentioned in the context of each transducer structure. CMOS-technology is then introduced as platform technology, which allows the fabrication of microtransducers and, moreover, enables the integration of these microtransducers with the necessary driving and signal conditioning circuitry on the same chip. Several examples such as microcapacitors, microcalorimeters, microcantilevers, and microhotplates are described in great detail. In a next step, the development of monolithic multisensor arrays and fully developed microsystems with on-chip sensor control and standard interfaces is depicted. A short section on packaging shows that techniques from the semiconductor industry can also be applied to chemical microsensor packaging. The book

concludes with a short outlook to future developments such as developing more complex integrated microsensor systems and interfacing biological materials such as cells with CMOS microelectronics.

As with all interdisciplinary efforts, teamwork plays a central role in being successful. Therefore I am particularly grateful to many colleagues and former students, who contributed much to the work that is the topic of this book. I would like to thank Prof. Henry Baltes for giving me the opportunity and the support to enter in the field of CMOS-based sensors in his laboratory. I very much appreciated his continual interest in discovering new things and exploring new fields of science. I am also very grateful to Prof. Oliver Brand, who was always a valuable source of information on microtechnology and microfabrication. I am very much obliged to several highly motivated and excellent coworkers, whose work is amply cited in this book: Christoph Hagleitner and Kay-Uwe Kirstein, the chief circuit designers, the microhotplate group: Markus Graf, Diego Barrettino, Stefano Taschini, Urs Frey, and Martin Zimmermann, the guys working on cantilevers: Dirk Lange, Cyril Vancura, Yue Li, Jan Lichtenberg, the capacitor freaks: Andreas Koll, Adrian Kummer, the microcalorimeter people: Nicole Kerness and Petra Kurzawski, and, finally, Wan Ho Song, who did the microsensor packaging.

In the outlook some first results on the combination of microelectronics and cells are mentioned. These rely on the work of Flavio Heer, Wendy Franks, Sadik Hafizovic, Robert Sunier, and Frauke Greve. I am very grateful for all their efforts, and I am looking forward to exciting new results in this research area.

I am also indebted to European collaboration partners, Udo Weimar and Nicolae Barsan, University of Tübingen, and to AppliedSensor GmbH, Reutlingen, who provided many of the chemically sensitive materials such as the metal oxides. The fruitful collaboration with Sensirion AG, Zürich, namely Felix Mayer and Mark Hornung, is also gratefully acknowledged.

Financial support for the CMOS chemical-sensor projects came from the European Union (FP5, FP6, IST-program), the Swiss Bundesamt für Bildung und Wissenschaft (BBW), the Swiss Commission for Technology and Innovation (CTI), and the Körber Foundation, Hamburg, Germany.

Zurich, September 2004

Andreas Hierlemann

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1 Introduction

The detection of molecules or chemical compounds is a general analytical task in the efforts of chemists to obtain qualitative and/or quantitative time- and spatially resolved information on specific chemical components [1]. Examples of *qualitative information* include the presence or absence of certain odorant, toxic, carcinogenic or hazardous compounds. Examples of *quantitative information* include concentrations, activities, or partial pressures of such specific compounds exceeding, e.g., a certain threshold-limited value (TLV), or the lower explosive limits (LEL) of combustible gases.

All this information can, in principle, be obtained from either a chemical analysis system or alternatively by using chemical sensors. In both cases sampling, sample pretreatment, separation of the components and data treatment are the tasks to be fulfilled. The main components of a state-of-the-art chemical analysis or sensor system are depicted schematically in Fig. 1.1.

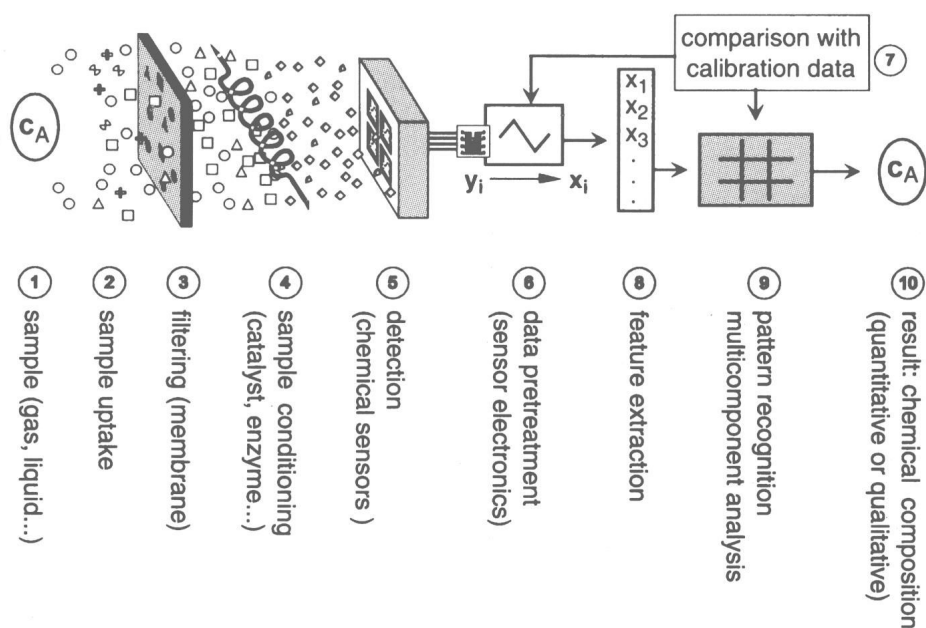


Fig. 1.1. Components of a chemical analysis or sensor system. Adapted from [15]

It is not easy to clearly distinguish between a chemical sensor and a complex analytical system. Integrated or miniaturized chromatographs or spectrometers may be denoted chemical sensors as well. However, a typical chemical sensor is, in most cases, a cheaper, smaller, and less complex device as compared to miniaturized analytical systems. A draft of the IUPAC (International Union of Pure and Applied Chemistry) provides a definition of a chemical sensor [2]: “A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal”. This rather wide definition does not require that the sensor is continuously operating and that the sensing process is reversible. But intermittently operating devices exhibiting irreversible characteristics are usually referred to as dosimeters [3]. In this context it is useful to introduce some important keywords used extensively throughout the chemical sensor literature [1, 4–11].

Reversibility

Thermodynamic reversibility, strictly speaking, requires that the sensor measurand is related to a thermodynamic state function. This implies that, e.g., a certain sensor response unequivocally corresponds to a certain analyte concentration (analyte here denotes the chemical compound to be monitored). The sensor signal may not depend on the history of previous exposures or how a certain analyte concentration is reached (no memory effects or hysteresis). More details on fundamental thermodynamics of the chemical sensing process will be given in Chap. 2.

Sensitivity and Cross-Sensitivity

Sensitivity usually is defined as the slope of the analytical calibration curve, i.e., how largely the change in the sensor signal depends upon a certain change in the analyte concentration. Cross-sensitivity hence refers to the contributions of compounds other than the desired compound to the overall sensor response.

Selectivity/Specificity

Selectivity or specificity can be defined according to Janata [4] as the ability of a sensor to respond primarily to only one species in the presence of other species (usually denoted as interferants).

Limit of Detection and Limit of Determination

The limit of detection (LOD) corresponds to a signal equal to k -times the standard deviation of the background noise (i.e., k represents the signal-to-noise ratio) with a typical value of $k = 3$. Values above the LOD indicate the presence of an analyte, whereas values below LOD indicate that no analyte is detectable.

The limit of determination implies qualitative information, i.e., that the signal can be attributed to a *specific* analyte. This in turn requires more information and, therefore, the limit of determination is always higher than the limit of detection.