

Novel Organic Membrane-based Thin-film Microsensors for the Determination of Heavy Metal Cations

Hassan A. Arida ^{1,*}, Joachim P. Klock ^{2,3} and Michael J. Schöning ^{2,3}

¹ Hot Laboratory Center, Atomic Energy Authority, 13759 Cairo, Egypt

² Aachen University of Applied Sciences Jülich Campus, Laboratory for Chemical Sensors and Biosensors, 52428 Jülich, Germany

³ Research Centre Jülich GmbH, Institute of Thin Films and Interfaces (ISG-2), 52425 Jülich, Germany.

* Author to whom correspondence should be addressed. Email: aridaha@hotmail.com

Received: 5 September 2005 / Accepted: 4 January 2006 / Published: 7 April 2006

Abstract: A first step towards the fabrication and electrochemical evaluation of thin-film microsensors based on organic PVC membranes for the determination of Hg(II), Cd(II), Pb(II) and Cu(II) ions in solutions has been realised. The membrane-coating mixture used in the preparation of this new type of microsensors is incorporating PVC as supporting matrix, o-nitrophenyloctylether (o-NPOE) as solvent mediator and a recently synthesized Hg[dimethylglyoxime(phenone)]²⁺ and Bis-(4-hydroxyacetophenone)-ethylenediamine as electroactive materials for Hg(II) and Cd(II), respectively. A set of three commercialised ionophores for Cd(II), Pb(II) and Cu(II) has been also used for comparison. Thin-film microsensors based on these membranes showed a Nernstian response of slope (26-30 mV/dec.) for the respective tested cations. The potentiometric response characteristics (linear range, pH range, detection limit and response time) are comparable with those obtained by conventional membranes as well as coated wire electrodes prepared from the same membrane. The realisation of the new organic membrane-based thin-film microsensors overcomes the problem of an insufficient selectivity of solid-state-based thin-film sensors.

Keywords: Heavy metal detection, thin-film microsensors, organic PVC membranes, potentiometry.

Introduction

The development of miniaturised and micro-sized ion-selective electrodes (ISEs) and their applications in many fields of analytics becomes a very essential challenge. These electrochemical sensors will be mostly benefit from the rapidly advancing technology. In other words, miniaturisation can be regarded as one aspect of the development of electrochemical sensors [1-3]. ISEs have been prepared with micropipette tips of the size in the order of micrometers.

With regard to a simple miniaturisation of ISEs, there is no doubt that the coated wire approach is an attractive one, too [4-10]. With a further miniaturisation and integration, microchip devices as well as microfabricated thin-film sensors and sensor arrays are among the most powerful tools for research in modern biotechnology [5]. Basically, they have mainly been used in biomedical research to assess the activity of various ions in living cells as well as in capillary electrophoresis, chromatography and in environmental research. The advantages brought by these new electrodes are a reduced size and small sample volume. Furthermore, the integration of sensors can be realised easily for a multi-analyte detection.

The selectivity and sensitivity of these microelectrodes were found to be comparable with those of conventional macro ion-selective electrodes based on the same ionophore. Most of these types showed good dynamic characteristics and were successfully used in a flow-injection analysis. In some of the cases, response becomes faster and fabrication costs are reduced compared with their macroscopic counterparts. Therefore, they can replace the classical ISEs in many applications [11,12].

A first step towards a microfabricated potentiometric thin-film sensor array for the simultaneous detection of Pb^{2+} , Cd^{2+} and Cu^{2+} has been reported using silicon planar technology [13]. The sensitive layers used were on the basis of chalcogenide glass materials. On the other hand, the manufacture and testing of a humidity sensor based on a combination of $\text{In}_2\text{O}_3/\text{SiO}$ as well as electronic tongues and their applications in analytical chemistry has been reported [14,15]. A pH sensor, fabricated by means of thin-film technique and a thick-film fabricated reference electrode were also integrated on a common printed circuit board [16-20]. A new design for microelectrode array (MEA) devices fabricated by semiconductor-processing techniques has been also presented [21,22]. The microelectrode surfaces of this array consisted of gold and were surrounded by an insulating silicon nitride layer. Furthermore, indium tin oxide (ITO) thin films have been extensively used as transparent conducting electrodes [23,24]. Tantalum nitride (TaN), zirconium oxide (ZrO_2) and gadolinium oxide (Gd_2O_3) have been used in preparation of a thin-film electrode using etching technique [25]. A less expensive and highly desirable electrical detection of biomolecules using thin-film electrodes has been also developed. These electrodes involved less complicated and less expensive instrumentation and similar detection limits compared to the traditional optical methods [26,27].

However, most of these solid-state-based thin-film sensors suffer from an insufficient selectivity. To solve this problem in terms of realising thin-film sensors with an enhanced selectivity, organic PVC-based membranes are used for the first time as a sensitive layer in a novel concept. These electrodes can be simply realised by applying PVC-based membranes sensitive to Cd(II), Pb(II), Cu(II) and Hg(II) on the thin-film metal contact (Au and Pt). The results obtained showed that the response characteristics of the new thin-film microsensors are comparable with those obtained by conventional

membrane-based electrodes as well as of those obtained by coated Ag wire-based electrodes, which are prepared from the same ionophore for the respective tested cations.

Experimental

Reagent and ionophores

Both commercialised and recently synthesized electrochemically sensitive materials have been used. The nature and the source of these sensitive materials are summarized in Table 1. All other salts and membrane components (analytical-reagents grade), namely, high molecular weight (poly vinyl chloride) (PVC), ortho-nitrophenyloctylether (o- NPOE), and tetrahydrofuran (THF) were purchased from Fluka (Buch, Switzerland). All standard solutions were prepared with bi-distilled deionized water by dilution of a freshly prepared stock solution using variable Eppendorf micropipettes.

Table 1. Sensor ionophores.

No.	Sensor	Ionophore	Source
1	Mercury (II)	Hg[dimethylglyoxime(phen)] ²⁺	Recently synthesized in our lab.
2	Cadmium (II)	Bis-(4-hydroxyacetophenone)-ethylenediamine	Recently synthesized in our lab [28].
3	Cadmium (II)	ETH 1062; N, N, N', N'-Tetra butyl-3,6-dioxaoctandi (thioamide)	Commercialised, purchased from Fluka.
4	Copper (II)	O-xylylene bis(N,N-diisobutyl dithiocarbamate)	Commercialised, purchased from Fluka.
5	Lead (II)	ETH 322; N,N,-Dioctadecyl-N', N'-dipropyl-3,6-dioxaoctandi amid	Commercialised, purchased from Fluka.

Metal coated thin-film substrates

Silicon wafers (3") with a specific resistance of > 1000 Ω cm and a thickness of 381 μm were used as the substrate material for the thin-film electrodes. Onto the silicon wafer, a SiO₂ insulating layer with a thickness of 500 nm was grown up by means of a thermal wet oxidation process. To structurize the wafer with the respective electrode structure, a positive photoresist (AZ5214, Hoechst) was applied via spin-coating. After the exposure through a photomask, the photoresist was directly developed with a developing solution (AZ 312 MIF, Clariant). The different metallic contacts were prepared by means of an electron-beam evaporation process. For the metallic and electrical contact, two layer systems (Ti: 15 nm/Pt: 200 nm and Ti: 15 nm/Pt: 150 nm/Au: 250 nm) were fabricated. With a lift-off process the unused metal part was removed. After cutting the wafer into the respective sensor chips with a size of

20 mm x 10 mm, the sensor chips were glued onto a printed circuit board (PCB). The electrical connection to the PCB was done by means of an Al foil and Ag paste. As a final step, the sensor chips were encapsulated with an epoxy resin.

Organic membrane-based thin-film microsensor fabrication

The ionophores were purchased or prepared as specified in Table 1 and were used as sensing material for the investigated metal cations. A stock solution of a cocktail-coating mixture was individually prepared for each ionophore by mixing 10 mg ionophore, 350 mg o-NPOE and 190 mg PVC in 6 ml THF. About 10 μ l of the homogenous coating mixture was evenly spread over the metal contact substrate (Pt and Ag). After evaporation of the solvent, this process was repeated until a uniform layer was obtained on the substrate and was allowed drying for 48 h. After drying, the sensor was soaked for one hour in a 10^{-2} mol l^{-1} solution of the respective tested cation. The stock solution of the cocktail-coating mixture was used to generate the sensor easily every day.

Thin-film microsensors evaluation

The potentiometric response characteristics of each sensor were evaluated according to IUPAC recommendations in terms of ionic sensitivity, detection limit, working concentration range, response time and life time [29]. The potential changes of the microsensor were measured against a Ag/AgCl reference electrode using a HANA (model 8417) pH/mV meter. All measurements were taken at ambient room temperature 25 ± 0.5 °C. During the measurements the sample was stirred using a magnetic stirrer.

Results and discussion

In the present study, the specified ionophores (Table 1) were investigated as sensing materials - in organic PVC membranes - for the respective cations. Our goal here is the realization of novel thin-film microsensors with enhancement selectivity. This was achieved by applying a well-known commercialised selective organic membrane as well as a recently synthesized selective organic membrane on a metal contact (Pt and Au) thin-film substrate to overcome the poor selectivity of solid-state-based thin-film sensors. Many comparison studies were performed for this purpose. Two thin-film microsensors were individually prepared for each ionophore using both Au and Pt metal contact substrates. Moreover, a conventional membrane-based electrode as well as a coated graphite rod-based electrode were also prepared for each ionophore. The thin-film microsensors, the coated rod electrodes and the conventional membrane electrodes for each ionophore were independently characterised for comparison.

For all tested ionophores, the results obtained showed that the potentiometric response characteristics (slope, detection limit, linear range, pH range and response time) of the thin-film microsensors based on Au and Pt substrates are nearly the same and are also comparable with those obtained by graphite rod- and conventional membrane-based electrodes.

All of the above mentioned different microsensors and macroelectrodes have been potentiometrically characterised. A data of some selected examples (not all) are presented in the

following sections for simplicity. Although the life time of the thin-film sensors is relatively short (one working day), they can be simply regenerated every day using the stock solution of the cocktail-coating mixture. After the life-time period, the slope is dimensioned and the response characteristics are not reproducible. This was attributed to the formation of a solid layer on the surface of the metal contact behind the organic membrane. The regeneration of the thin-film microsensor is achieved easily by removal of the organic membrane, cleaning the solid layer and applying a new organic membrane on the clean metal-contact surface.

Mercury (II) thin-film microsensors

Fig. 1 shows a typical calibration curve of the developed mercury thin-film microsensors based on the $\text{Hg}[\text{dimethylglyoxime(phen)}]^{2+}$ ionophore using both Au and Pt metal contact substrates. For comparison, the potentiometric response of the mercury graphite rod electrode based on the same ionophore is also presented. The properties of the three sensors are comparable and may be characterised by the following parameters: sensitivity 28-30 mV per decade, range of linear response from 1.0×10^{-1} to 1.0×10^{-6} mol l^{-1} , and detection limit of 4×10^{-7} - 7×10^{-7} mol l^{-1} . It must be noted that the potentiometric response characteristics of the suggested thin-film microsensors are in good agreement with those obtained by the graphite rod-based mercury macroelectrode prepared from the same membrane. However, the new mercury thin-film microsensors offer the advantages of miniaturisation, integration and good selectivity.

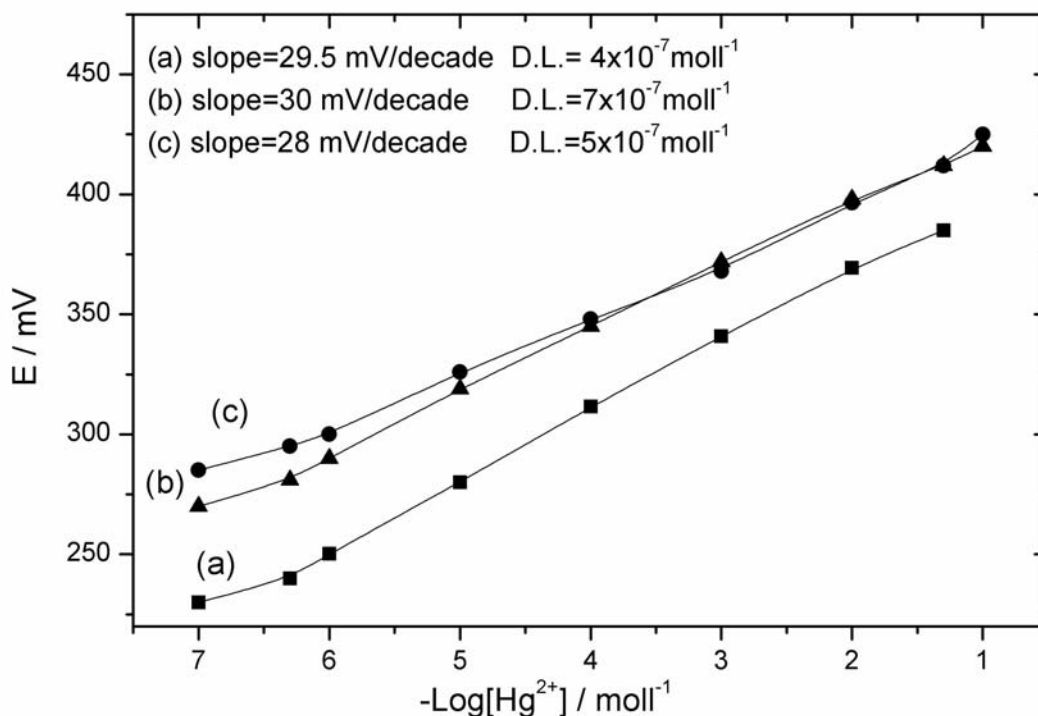


Figure 1. Potentiometric calibration graph of mercury-sensitive electrodes; (a: graphite rod, b: Au microsensor, c: Pt microsensor).

Cadmium (II) thin-film microsensors

In our previous work, a bis-(4-hydroxyacetophenone)ethylenediamine cadmium complex has been prepared [28] and used in the PVC membrane as sensing material for a cadmium(II) graphite rod-based macrosensor. This ionophore was used here in the preparation of both the thin-film microsensors and the graphite rod-based electrode. The potentiometric response of the new cadmium thin-film microsensor is presented in Fig. 2. For comparison, the calibration curve of the cadmium graphite rod-based electrode is also presented. It can be seen that the potentiometric properties such as response slope, linear range, detection limit and response time obtained with both the thin-film microsensors and the graphite rod macrosensor are approximately the same. The thin-film microsensors provide a Nernstian response for cadmium covering the concentration range of 1×10^{-1} – 1×10^{-6} mol l⁻¹ with a slope of 27–29 mV per cadmium concentration decade, a detection limit of 1×10^{-6} – 7×10^{-7} mol l⁻¹ and a response time of 40 s. These results are also in good agreement with those obtained by conventional membrane-based cadmium(II) electrodes based on the same ionophore [28]. However, the new thin-film cadmium(II) microsensors based on the organic membrane offer the advantages of a good selectivity, miniaturisation and integration.

A further realization of thin-film microsensors based on organic membranes has been achieved using the commercialised cadmium(II) ionophore (ETH 1062; N, N, N', N'-Tetra butyl-3,6-dioxaoctanedi (thioamide) as sensing material for cadmium(II) in a PVC organic membrane-based thin-film microsensor. The results obtained (Table 2) showed that the thin-film microsensor based on this ionophore provides a Nernstian response for cadmium(II) with a slope of 29 mV/concentration decade covering the range 1×10^{-5} – 1×10^{-2} mol l⁻¹, a detection limit of 5×10^{-6} mol l⁻¹ and a response time <40 s. These results are approximately the same to those obtained with a silver wire-based electrode prepared from the same membrane.

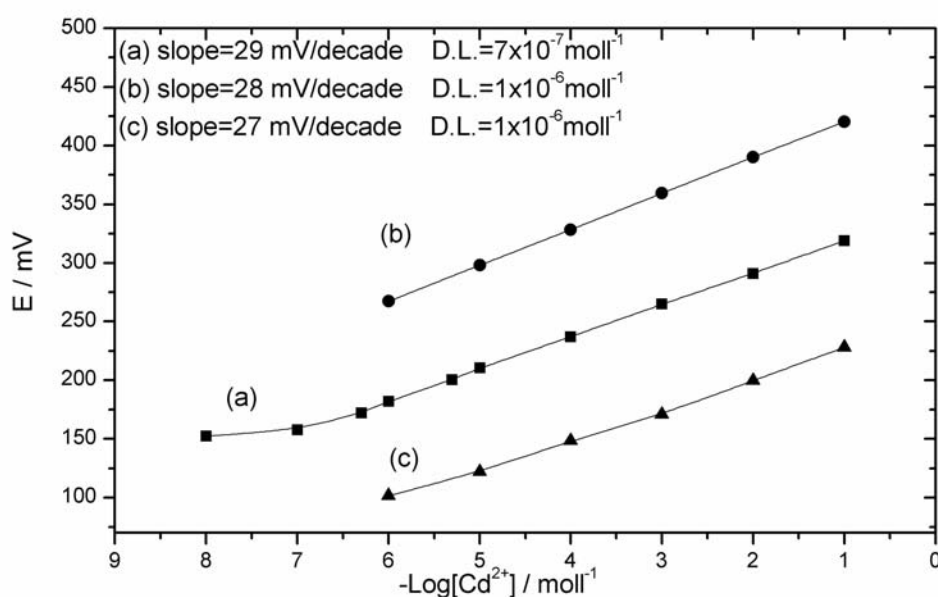


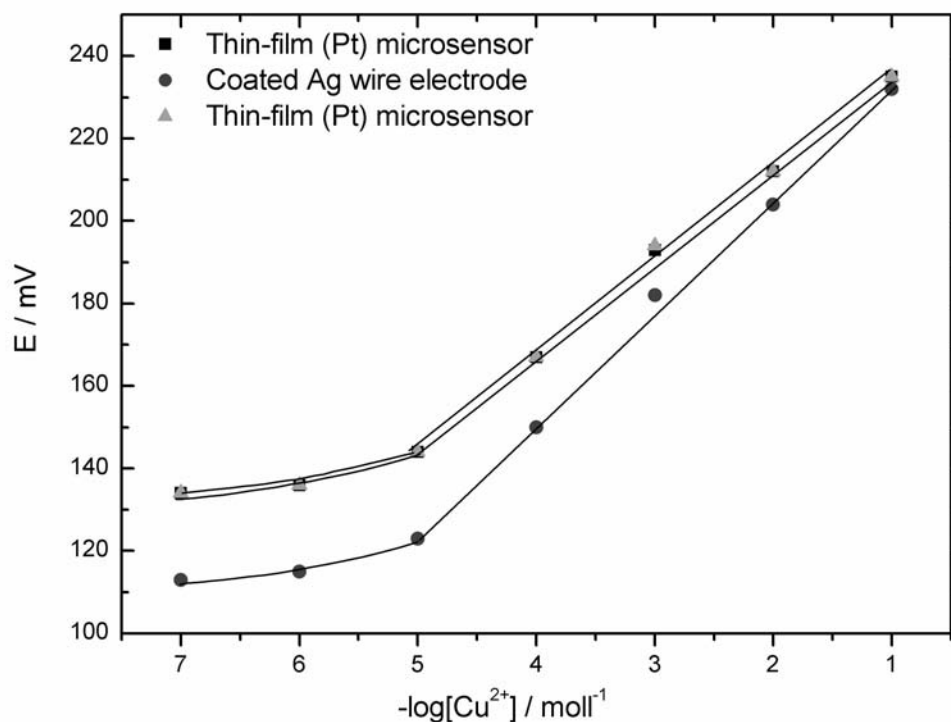
Figure 2. Potentiometric calibration graph of the cadmium-based Bis-(4-hydroxyacetophenone)-ethylenediamine electrode (a: graphite rod, b: Pt microsensor, c: Au microsensor).

Table 2. Characteristics of ionophore-based (ETH 1062) thin-film cadmium microsensor.

Parameter	Cadmium sensor
Slope (mV/decade)	29 ± 0.5
Linear range (mol l^{-1})	1×10^{-5} - 1×10^{-2}
Detection limit (mol l^{-1})	5×10^{-6}
Response time (s)	<40

Copper (II) thin-film microsensors

To confirm the possibility of realization of a future type thin-film microsensor, *o*-xylylene bis(*N,N*-diisobutyl dithiocarbamate) has been used as electroactive material for Cu^{2+} ions in an organic PVC membrane. For comparison, two different metal-contact (Pt) substrate microsensors based on two different preparations using the copper ionophore have been prepared and electrochemically investigated. For this purpose, a coated wire-based (Ag) electrode has been also prepared and characterised. Fig. 3 presents the response of the three copper electrodes. As can be seen, the potentiometric response characteristics of the two thin-film microsensors are nearly the same and are in good agreement with the results obtained with the coated Ag wire electrode.

**Figure 3.** Potentiometric calibration graph of the Cu(II) thin-film microsensors based on PVC membranes.

The new thin-film copper microsensors reveal a near-Nernstian linear response covering the range of 1×10^{-1} - 1×10^{-5} mol l⁻¹ with a slope of 26 mV per concentration decade and a detection limit of 5×10^{-6} mol l⁻¹.

Lead (II) thin-film microsensors

In order to extend the technology for preparing thin-film PVC-based microsensors, additionally a Pb(II) electrode was prepared and preliminary investigated. Potentiometric properties such as response slope, linear range, detection limit and response time are determined for the new lead thin-film microsensor and the results are summarized in Table 3. These results are comparable to those obtained with a coated Ag wire electrode prepared from the same membrane.

Table 3. Characteristics of thin-film lead microsensor.

Parameters	Lead sensor
Slope (mV/decade)	26.5
Linear range (mol l ⁻¹)	1×10^{-2} - 5×10^{-6}
Detection limit (mol l ⁻¹)	1×10^{-6}
Response time (s)	<30

Conclusions

A novel type of thin-film chemical microsensor for some divalent metal cations (Hg²⁺, Cu²⁺, Pb²⁺, and Cd²⁺) has been developed by the methods of silicon planar technology using PVC-based organic membranes. These metal-contact (Pt & Au) microsensors based on a set of commercially available and recently synthesized ionophores for the tested cations were independently prepared and electrochemically evaluated. The results obtained showed that the response characteristics of all investigated organic membrane-based thin-film microsensors are comparable with those obtained by conventional membrane-based electrodes as well as of those obtained by coated Ag wire-based electrodes, which have been prepared from the same ionophore for the respective tested cations. The realization of the new organic membrane-based microsensors enhances the selectivity of the solid-state-based thin-film sensors. Although the life time of the suggested microsensors is relatively short (one working day), they can be reactivated easily every day using a stock solution of the cocktail-coating mixture prepared for this purpose.

Acknowledgements

The authors gratefully thank the Ministerium für Innovation, Wissenschaft, Forschung und Technologie des Landes Nordrhein-Westfalen and Deutsche Forschungsgemeinschaft for financial support.

References

1. Feeney, R.; Kounaves, P. Microfabricated ultramicroelectrode array: developments, advances, and applications in environmental analysis. *Electroanalysis*, 2000, 12, 677.
2. Economou, A.; Fielden, P.R. Mercury film electrodes: developments, trends and potentialities for electroanalysis. *Analyst*, 2003, 128, 205.
3. Miller, A.J.; Cookson, S.J.; Smith, S.J.; Wells, D.M. The use of microelectrodes to investigate compartmentation and the transport of metabolised inorganic ions in plants. *Experimental Botany*, 2001, 52, 541.
4. Bendikov, T.A.; Kim, J.; Harmon, T.C. Development and environmental applications of a nitrate microsensor based on doped polypyrrole film. Technical Report No. 14, Center For Embedded Networked Sensing, 2003.
5. Golabi, S.M.; Mohammadi, J. Wire-coated silver(I) ion-selective electrode based on 2-mercaptobenzothiatole (MBT) ionophore: application to the determination of silver in real samples. *Anal. Sci.*, 2003, 19, 877.
6. Tanaka, Y.; Sato, K.; Yamato, M.; Okano, T.; Kitamori, T. Drug response assay system in a microchip using Human hepatoma cells. *Anal. Sci.*, 2004, 20, 411.
7. Carden, D.E.; Diamond, D.; Miller, A.J. An improved Na⁺-selective microelectrode for intracellular measurements in plant cells. *J. Exp. Botany*, 2001, 52, 1353.
8. Tokeshi, M.; Kikutani, Y.; Hibara, A.; Sato, K.; Hisamoto, H.; Kitamori, T. Chemical processing on microchips for analysis, synthesis, and bioassay. *Electrophoresis*, 2003, 24, 3583.
9. Yun, M.; Myung, N.V.; Vasquez, R.P.; Lee, C.; Menke, E.; Penner, R.M. Electrochemically grown wires for individually addressable sensor array. *J. Nano Lett.*, 2004, 4, 419.
10. Yun, M.; Myung, N.V.; Vasquez, R.P.; Wang, J. *Nanofabrication Technologies*. Ed. E. A. Dobisz, SPIE Proceedings, 2003, 522.
11. Suzuki, H. Advances in the microfabrication of electrochemical sensors and systems. *Electroanalysis*, 2000, 12, 703.
12. Cai, X.; Glidle, A.; Cooper, J. M. Miniaturized electroanalytical sensor system in microchemical structures. *Electroanalysis*, 2000, 12, 631.
13. Kloock, J.P.; Mourzina, Y.G.; Schubert, J.; Schöning, M.J. A first step towards a microfabricated thin-film sensor array on the basis of chalcogenide glass materials. *Sensors*, 2002, 2, 356.
14. Arshak, K.; Twomey, K. Thin films of In₂O₃/SiO for humidity sensing applications. *Sensors*, 2002, 2, 205.
15. Vlasov, Y.; Legin, A.; Rudnitskaya, A. Electronic tongues and their analytical application. *Anal. Bioanal. Chem.*, 2002, 373, 136.

16. Simonis, A.; Krings, T.; Lüth, H.; Wang, J.; Schöning, M.J. A hybrid thin-film pH sensor with integrated thick-film reference electrode. *Sensors*, 2001, 1, 183.
17. Simonis, A.; Lüth, H.; Wang, J.; Schöning, M.J. Strategies of miniaturized references electrodes integrated in a silicon based 'one chip' pH sensor. *Sensors*, 2003, 3, 330.
18. Schöning, M.J.; Mourzina, Yu.G.; Schubert, J.; Zander, W.; Legin, A.; Vlasov, Yu. G.; Lüth, H. Pulsed laser deposition - an innovative technique for preparing inorganic thin films. *Electroanalysis*, 2001, 13, 727.
19. Schöning, M.J.; Mourzina, Yu.G.; Schubert, J.; Zander, W.; Legin, A.; Vlasov, Yu.G.; Lüth, H. Can pulsed laser deposition serve as an advanced technique in fabrication chemical sensors? *Sensors and Actuators B*, 2001, 78, 273.
20. Schöning, M.J.; Simonis, A.; Krings, T.; Lüth, H.; Wang, J. Evaluation of a chip-based thin-film/thick-film sensor hybrid for (bio-) chemical analysis. *Electroanal.*, 2001, 14, 955.
21. Kudera, M.; Hill, H.A. O.; Dobson, P.J.; Leigh, P.A.; McIntire, W.S. Electrochemical characterisation and application of multi microelectrode array devices to biological electrochemistry. *Sensors*, 2001, 1, 18.
22. Den Otter, M. Approximate expression for the capacitance and electrostatic potential of interdigitated electrodes. *Sensors and Actuators A*, 2002, 96, 140.
23. Sako, T.; Ohmi, A.; Yumoto, H.; Nishiyama, K. ITO-film gas sensor for measuring photodecomposition of NO₂ gas. *Surface and Coatings Technology*, 2001, 142, 781.
24. Jiao, Z.; Wu, M.; Qin, Z.; Lu, M.; Gu, J. The NO₂ sensing ITO thin films prepared by ultrasonic spray pyrolysis. *Sensors*, 2003, 3, 285.
25. Tonotani, J.; Takagi, S.; Ohmi, S.; Iwai, H. Reactive ion etching of TaN for a metal gate electrode and ZrO₂ and Gd₂O₃ for high-k gate insulators. 205th meeting, of the Electrochemical Society, Inc., 2004, 144.
26. Shimizu, M.; Ojima, N.; Ohanishi, H.; Shingaki, T.; Hirakawa, Y.; Masujima, T. Development of the single-cell MALDI-TOF (matrix-assisted laser deposition/ionization time-of-flight) mass-spectroscopic assay, *Anal. Sci.*, 2003, 19, 49.
27. Ma, K.-S.; Zhou, H.; Fischetti, A.; Zoval, A.; Madou, M. Electrical biosensor for label-free DNA hybridization detection. 205th meeting of the Electrochemical Society Inc., 2004, 901.
28. Arida, H.A.; El-Saied, A.M.; El-Reefy S.A. Cadmium(II)-selective membrane coated graphite electrode based on recently synthesized bis-(4-hydroxyacetophenone)-ethylenediamine, *Sensors*, 2004, 4, 43.
29. Buck, R.P.; Lindner, E. Recommendations for nomenclature of ion-selective electrodes, *Pure Appl. Chem.*, 1994, 66, 2527.