THIN-FILM ELECTRODE CHIPS FOR MICROELECTROCHEMICAL SENSORS

Vladimir Tvarozek, Ivan Novotny, Vlastimil Rehacek, Rastislav Ivanic, Fedor Mika

Thin-film microelectrodes on Si-chips were manufactured for using as electrochemical microprobes. Forming of lipid bilayers on planar chips with thin-film electrodes has opened up new possibilities for the development of miniaturized biosensors as well as for basic research on electrical and mechanical properties of biological membranes. A simple portable pH-meter for different types of pH- and/or ion-probes was developed and tested for use with the lipid bilayer-based microprobes.

1. Introduction

The demand for fast, one-purpose and reliable measurements in chemistry, medicine, biotechnology and environment has evolved the need for small, easy to handle and inexpensive (bio)chemical analytic devices. Electrochemical sensors are one of the largest groups of (bio)chemical sensors and the combination of microelectronics and electrochemistry brings the new microelectrochemical devices with improving characteristics and low prices. Thin films are able to create „the bridge" between macrosystems and microsystems down to molecular systems, *i.e.* the research and development of advanced microelectrochemical sensors cannot endure without the utilization of thin film technology. The role of thin films in planar microelectrochemical biosensors can be divided into two categories: (1) thin film microelectrodes serve as a base array in electrochemical cell; working/auxiliary Pt, Au, C, reference Ag/AgCl electrodes (in compact, microdisk or interdigitated array (IDA) forms); (2) sensitive inorganic-, organic- and biomaterials (like membranes, enzymes, receptors, antibodies) are used (or immobilized) in the form of thin films.

A constituent of the living cell membrane - Bilayer Lipid Membrane (BLM) - seems to be a very "advanced" material for biosensors and bioelectronics. Most of the vital cellular functions such as energy transduction, sensory perception, and information processing take place in membranes of the cell and its organelles. The biomembrane is best described as a two-dimensional, liquid-crystalline (smectic) structure of lipids and other constituents. The lipids of biomembranes are self- organised in the form a bilayer of the thickness of about 6 nm. Great acceleration of possible applications has been caused by the invention of a self - assembled BLM on a solid support (s-BLM) [1]. Today's BLMs are successfully formed also on thin-film electrodes which create the necessary "bioelectronic" interface [2]. Of all the ions crucial to the functioning of cellular processes is the hydrogen ion (H+) which plays the leading role in enzyme catalysis and membrane transport. Thus, it is not surprising that, the measurement of pH (the negative logarithm of hydrogen ion concentration) is of the almost importance in chemical and clinical laboratories. This paper presents a selected output of our research activities in the domain of microelectrochemical sensors and analytic devices.

2. Planar thin-film electrode chips

Selected planar form of thin-film microelectrodes fabrication in our lab. are shown in Fig. 1. They serve as a base electrode array for conductometric / potentiometric/ voltammetric electrochemical sensors, and particularly as a thin-film support for lipid bilayers [3]. Two kinds of substrates have been used: alumina-boron-silica glass substrates and silicon wafers covered by passivating SiO_2 thin film of 300 - 800 nm in thicknesses. Deposition of thin films of Pt, Pd, Au, Ti, Ag was done by r.f. sputtering and for the patterning of thin-film structures UV photolitography combined with chemical/plasma etching and „lift-off" technique were used. Protective films were created by photoresist or polyimide. The polyimide was formed by spin-coating, baking and curing of the polyimide precur-

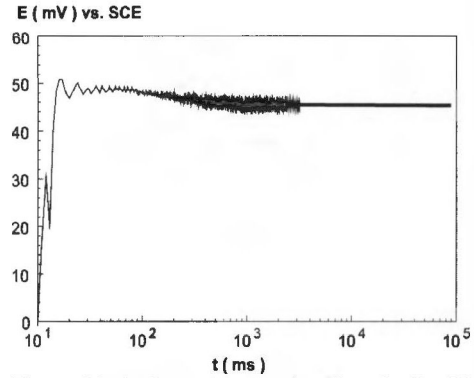

Fig. 2. Variation of the thin–film Ag/AgCl reference electrode potential (measured vs. SCE) in function of time at 25° C in 0.1 mol/l KCl.

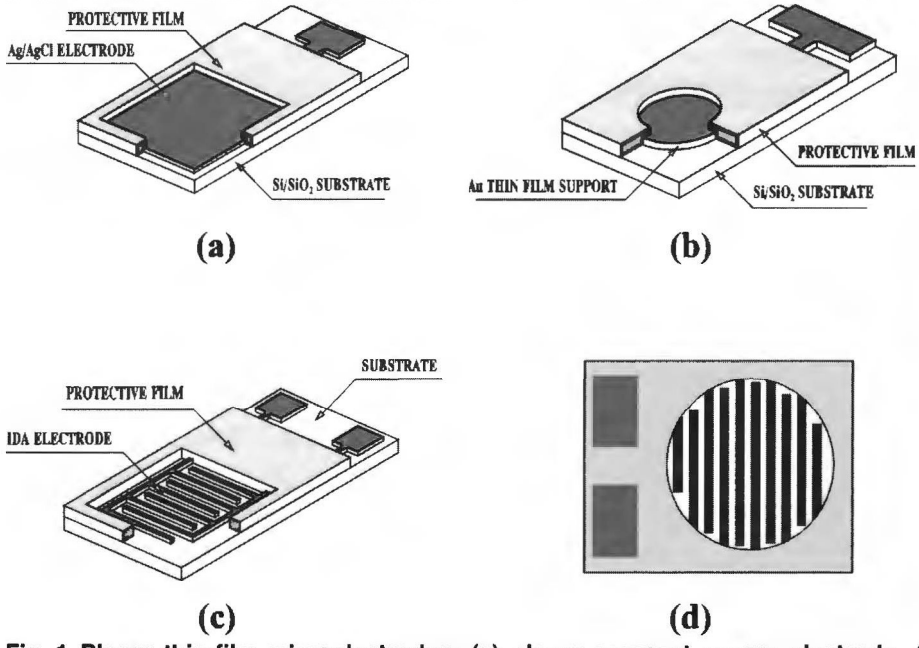

Fig. 1. Planar thin-film microelectrodes: (a) planar compact square electrode, (b) planar compact circle electrode, (c) IDA electrodes horizontally arranged, (d) IDA circle electrode.

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sor. The Si-substrate was sawed up to microelectrode chips in dimensions of 10 x 3 mm or 13 x 9 mm.

Compact electrodes have formed in the square (600 x 600 μm), rectangular (1266 x 1365 μm) or circular (∅ 700 μm) shapes. Two kinds of IDA electrodes has been manufactured: (1) IDA with finger/gap widths of 10/10 μm, 5/5 μm, 5/3 μm and rectangular shape window of electrode in dimensions of 600 x 600 μm or 1266 x 1365 μm; (2) IDA with finger/gap widths of 50/50 μm, 100/100 μm, 200/200 μm, 400/400 μm and circular shape window of electrode in diameter ∅ 6.5 mm (chip dimensions of 13 x 9 mm).

For a reliable response of an electrochemical sensor the reference electrode is of crucial importance. The thin-film Ag/AgCl electrode with good stability, reproducibility and repeatability has been developed [4]. After a period of about 1 sec. the potential electrode reached a steady-state value of +45.9 mV vs. SCE in 0.1M KCl (Fig. 2). A small negative drift of the potential over time was observed (-3 μV/s). Potential values repeatable measured over 5 days were dispersed around their average values by not more than 1.2%. The temperature dependence of Ag/AgCl electrode potential was 0.3 mV/°C in the range from 20 to 40° C.

3. Electrical properties of BLMs

Instead, the formation process of a s-BLM can be examined by monitoring its electrical properties, such as membrane capacitance and resistance. Recently, many new electrochemical methods have been developed and applied for the membrane research. Among them, the *cyclic voltammetry* (CV) technique has been found very powerful [5].

The PC simulator „BLMSim" has been developed for simulations of the electrical behaviours of BLMs and sl-BLMs. This simulator is working for Windows 95 and utilizing a program PSPICE (Electrical Circuit Simulator, Evaluation Version, Jan. 1989). In CV measurement on a conventional planar BLM system, the current-time (I-t) characteristics response of the BLM system is obtained. This type of cyclic voltammogram corresponds to the standard BLM equivalent circuit in which the membrane capacitance C_m ($\cong 10^{-12}$ F) is in parallel with the membrane resistance R_m ($>10^8$ Ω). R_m characterises the conductivity of the double layer, C_m is the capacitance a this double layers. If cyclic voltammetry is applied to the sl-BLM system, the current-time characteristic does not correspond to the I-t of the BLM system. The difference between them indicates that the standard equivalent circuit for BLM is not suitable for sl-BLM system. The sl-BLM system was described by a new equivalent circuit based on the standard BLM circuit. In addition there are the non-membrane resistance R_n in series with the standard circuit, and the parallel C_s. R_n is due to the metallic-lipid interface (interface resistance) and R_n likewise includes the electrode, electrolyte and solution impedance. C_s is the stray capacitance for the entire circuit. The membrane capacitance is also changed by the applied voltage (electrostriction effect) depending on the elasticity and volume compressibility of the BLM. Membranes are considered as a homogeneous isotropic solid with Young elasticity modulus and modulus of volume compressibility [6]. Computer simulations of sl-BLM's CV characteristics corresponded to the dependences given by experiments (Fig. 3).

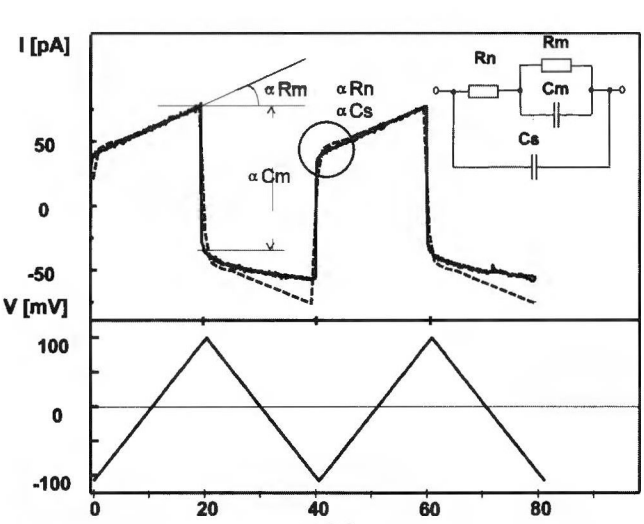

Fig. 3. Voltammograms of the sl-BLM (solid line - measured curve, dash line - simulated curve), C_m = 8.82 nF, R_m = 5.53 GW.

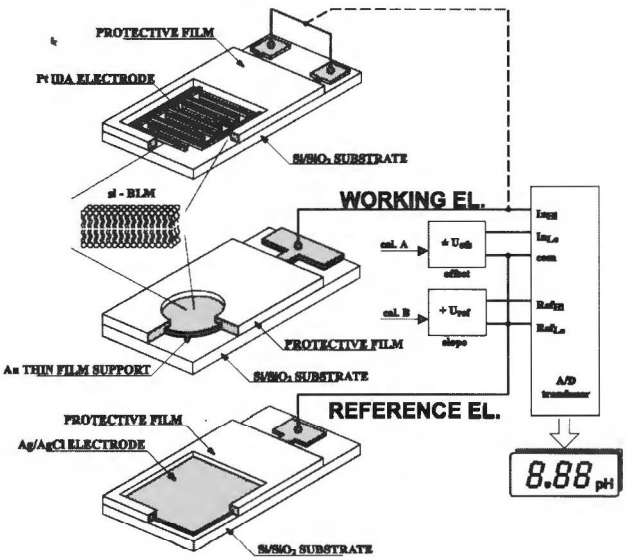

Fig. 4. Layout of pH-meter with thin-film sl-BLM/Au or Pt working and Ag/AgCl reference electrodes.

4. pH-meter with sl-BLM microprobe

We have designed and manufactured a portable pH-meter with a universal high resistance input adaptable for different kinds of pH-sensitive, or ion-selective electrodes, as well as for voltage and temperature measurements (Fig. 4). For realization of the pH-meter there were exploited the advantageous properties of integrated A/D transducer with input impedance $>10^{11}$ ohms. Calibration of the pH-meter proceeds in an adjustment of the sensitivity (-100 ÷ +100 mV/pH) and the offset (-750 ÷ +750 mV/pH) for the available type of electrode. This is possible by setting of two calibrating trimmers (cal. A, cal. B) and using two reference buffers solutions with known pH-values.

A thin-film microprobe was developed consisting of a thin-film Ag/AgCl reference electrode and a bilayer lipid membrane based Si-chip with Au or Pt thin-film electrodes. Unmodified sl-BLMs displayed low pH-sensitivities -13.5 mV/pH (Fig. 5). Membrane potential response of a TCOBQ (tetrachloro-o-benzoquine) - containing sl-BLM formed on Pt-IDA microelectrode chip to pH changes exhibited larger values of -49.2 mV/pH. The response of sl-BLM modified by TCNQ (tetraciano-p-quinodimethane) and prepared on Au-compact microelectrode chip to pH changes was also linear with a sensitivity of s = -60.9 mV/pH.

These results have proved that sl-BLMs doped by electron acceptor mediators generate changes of membrane potential depending on the H^+ concentra-

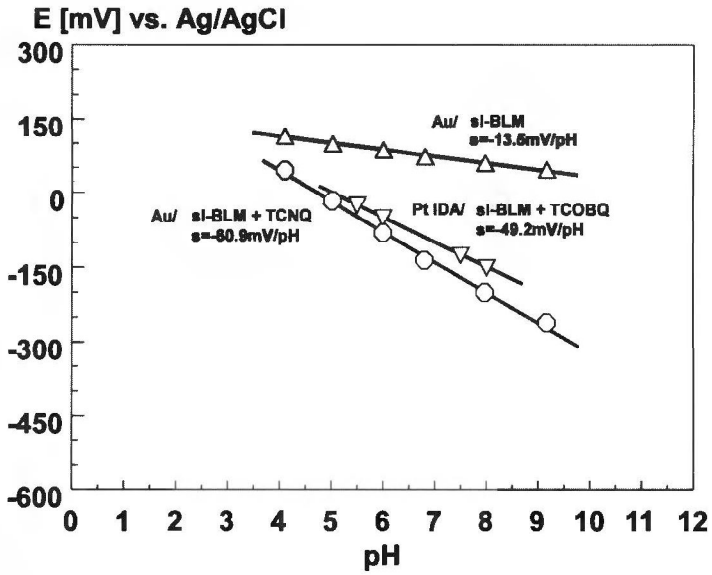

Fig. 5. Membrane potential responses of different microprobes on pH.

tion in the surrounding aqueous solution. Although intrisic BLMs are excellent insulators a suitable modification makes them ion-selective or electron conducting e.g. the pH sensitivity mediating substances TCNQ or TCOBQ create channel-like structures in the BLM which can be accessed by electrons. Stability of sl-BLMs formed on thin-film microelectrodes was tested by continual cyclic voltametric measurements during 24 hours. No changes in resistance and capacitance were observed. Except this, thin-film microprobe with sl-BLM can be used as a disposable "one shot" probe for handle instruments.

5. Conclusion

Planar thin-film electrode chips have been designed and manufactured that way to fulfil the maximum requirements for the most extensive utilization in research and development of electrochemical sensors. Solving the compatibility of BLMs with planar chips is essential for their future applications in the field of mikrobiosensors and bioelectronics.

Acknowledgement

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HIGH RESOLUTION NONCOOLED GAMMA RAY SPECTROMETRIC DETECTORS ON THE BASE CdTe(Cl) SINGLE CRYSTALS

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Features of CdTe (Cl) gamma ray detectors with a high energy resolution (<2%) in the region 60-1300 keV are described.

1. INTRODUCTION

Of the solid state sensors available, spectrometric CdTe ideally suited for variety of applications: high resolution room temperature tomography, portable γ-ray detector - spectrometer, pocket-sized coal dust incombustibles meter for mine safety, narcotics scanner, various medical diagnosis instruments, etc. According to the literature data the main limitation is the relative poor energy resolution. The best reported result of about 2% [1] has been obtained with a cooled CdTe detector. However, the detector cooling is not practicable for a widespread use.

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2. EXPERIMENTAL AND RESULTS

The crystals were grown by the vertical Bridgman method and were compensated with chlorine dope ($N_{Cl}=10^{18}$-$10^{19}cm^{-3}$). Additional purification of the CdTe source , original method of the doping, and programmed cooling of the ingots were applied. Under these technological conditions the useful yield per ingot was more than 60%.

We used planar metal-CdTe-metal structure for high resistivity (>10^9 Ohm×cm) CdTe sensors manufacturing and found the most suitable method of surface metallization to provide the high quality pulse height spectra. The energy resolution of these sensors was measured as a function of both bias volt-