3-D ELECTRODES DESIGN FOR THICK-FILM SENSORS

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Miniature electrochemical sensors can be produced using thick film technology (TFT). Fabrication technology optimization of thick-film sensors, the adjustment of optimal technological properties and especially the optimal properties of thick-film electrode materials and electrode topology are main problems of sensor design. The electrode topology design is one of very important parts. One method of working electrode area increasing on small sensor substrate with maintenance of sufficient rate between working electrode area size: reference electrode area size is possible by TFT paste elevations on basic electrode surface and optimization of topology. Some aspects about this problem are discussed in this paper.

Keywords: Thick-film sensor, electrochemical sensor, electrode.

1. INTRODUCTION

Thick-film sensors are used in various human activities (food industry, agricultural industry, automobile industry, medicine, …) . The main advantage of TFT is low price and small scale batch production [1]. At present time the TFT are used as a tool of preparation of very small electronic details by SMT [2], high reliability applications and nonconventional applications [3], especially sensors. TFT sensors are often simple, cheap, sufficiently sensitive and accurate, with good mechanical and electrical properties. But the application of thick film technology to chemical sensors and biosensors is complicated [4], [5]. Processes on electrodes of TFT electrochemical sensors are more complicated than in classical electrochemistry. Electrochemical methods are extremely sensitive, which means that even small impurity, which has negligible influence in classical sense, can influence the final sensitivity and other properties significantly. The materials of TFT electrodes are non-homogeneous from microscopic point of view (composition, structure...), they do not have well defined area, roughness of surface, etc.

The active area is bigger than the effective geometric area. Complicated geometric area can be an advantage or disadvantage depending on the measuring process. The smaller physical area is good for immunosensors whereas larger physical area is extremely important in case of immobilization of enzymes i.e. enzyme biosensors. Obtaining the larger physical area is very often case, which are researched. One way of working electrode area increasing on small sensor substrate is 3-D electrodes design. One of 3-D electrodes design methods is described in this paper, which is focused on the case of amperometric TFT sensors only.

2. BASIC INFLUENCE

The current output signal of amperometric sensor is depended on sensor design, materials, technological parameters of production, packaging, transport, storage and influences in measurement time (temperature, light, etc.). The materials of electrodes are non-homogeneous from microscopic point of view (composition, structure, etc.), they do not have well defined area, roughness of surface, etc.

The electrode system topology is very important problem in thick film sensor design too. In classical electrochemistry, the working electrode area A_{WE} is often defined by window in body electrode construction or by area of rod from various materials. The reference electrode area A_{RE} is defined from small window in body electrode construction, e.g. glass Ag/AgCl electrode for three-electrode system to large area of mercury reference electrodes in polarography for two-electrode system [6], [7]. The rate A_{WE}:A_{RE} is often 1:50 in classical polarography. The large reference electrode area is better for potential stability on electrode in two-electrode system [8].

The thick-film electrode topology design is limited (substrate dimensions, resolution, paste parameters). The rate A_{WE} : A_{RE} is often 1:10 and less. Therefore three electrode systems are made on TFT electrochemical sensors. The auxiliary electrode is often connected to reference electrode in case of two electrode system with use of three electrode sensor. The main aims of topology design are increase of work electrode area (I_{out} = f(A_{WE})) and increase of rate A_{WE}:A_{RE} (for potential stability). Because TFT electrode area is limited of substrate area, larger electrode area can be made by 3-D structure only. One of the solutions is creation of elevations on basic electrode surface. Basic idea is shown in fig. 1.

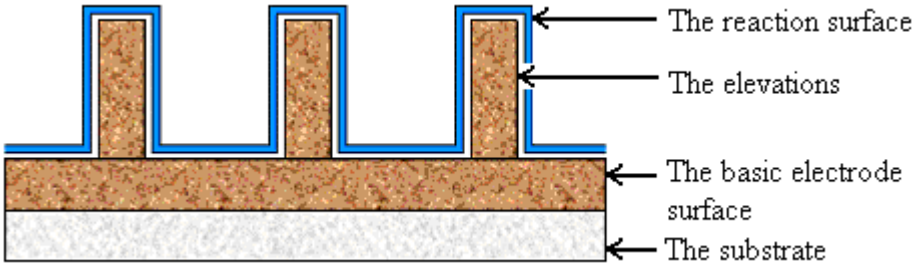
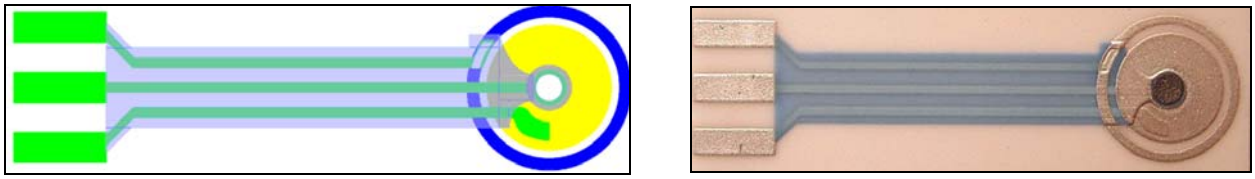


Fig. 1: Basic idea of 3D structure solution made by elevations.

The elevation can be made by thick-film technology. Although the high of elevations is equal to thick film paste thickness (tens of μm), the change of rate of working electrode area : reference electrode area is significant, because elevations may be more. Then total area increment is sum of the arisen area made by elevation.

3. SENSOR TOPOLOGY DESIGN

The basic shape and real sample of amperometric sensor, which was used for measurement, is shown in figure 2. The gold paste was used as working electrode material. Sensors type AC1 with Au and Pt working electrode from BVT Technologies, a.s., Brno [9], fig. 3, was used as commercial sensor for comparison. The area for electrode system is same for both sensors.



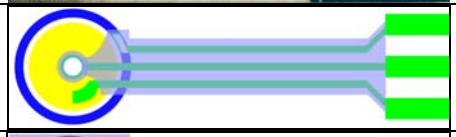
a, design b, real sample

Fig. 2: The amperometric sensor S1.

Fig. 3: Real sample of sensor AC1.W1.R1, [9].

The design of amperometric sensor is focused to make of 3D structure and optimize of rate A_{WE}:A_{RE}. Comparison of AC1 and S1 type sensors and some of possible sensor designs (D1-D4) are shown in tab. 1.

Tab. 1: Comparison of AC1 and S1 type sensors and some sensor designs (D1-D4).

Type	Figure	A_{WE}	A_{RE}	A_{AE}	Rate A_{RE}:A_{WE}	Rate (A_{RE}+A_{AE}):A_{WE}
AC1		0,780	14,560	9,410	18,667	30,731
S1		1,539	17,082	9,577	11,102	17,327
D1		1,130	20,186	8,761	17,858	25,608
D2 (S2)		1,130	20,186	15,193	17,858	31,298
D3		1,130	20,065	8,761	17,750	25,500
D4		3,140	23,546	7,620	7,499	9,925

The sensor design D2 has best rate A_{RE}: A_{WE} = 17,8:1 for three-electrode system and rate (A_{RE}+A_{AE}):A_{WE} = 31,3:1 for two-electrode system, when auxiliary electrode is connected to reference electrode. This rate is calculated from geometrical areas of electrodes including elevations. This design was chose as new amperometric sensor

type S2. The design and real sample of amperometric sensor S2 is shown in figure 4. The gold paste ESL 8844-G was used as work electrode material.

a, design b, real sample

Fig. 4: The amperometric sensor S2.

4. RESULTS

4.1. Objective

The objective of this work was the study of the electrode area influence to output current response of amperometric sensor using the standard detection of H_2O_2 and heavy metal (Cd). All compared sensors are designed on the same size of electrode area.

4.2. Chemicals and electrochemical experiment

The sensor was inserted into a Micro Flow System [9] which was connected to an analytical electrochemical workstation AEW2-10 [10]. The amperometric method (on constant potential of 650 mV) was used for all measurements. 50 mmol l^{-1} $Na_2B_4O_7$ in H_2O was used as a buffer solution. Buffer solution volume was 10 ml. Additions of hydrogen peroxide were added four times from the stock solutions to measurement system for each concentration of H_2O_2 (880 mmol l^{-1}, 88 mmol l^{-1} and 8,8 mmol l^{-1}). Addition volume was 50 µl. A calibration curve was made for sensor S1 and AC1 with gold working electrode.

Heavy metal detection was made by an analytical electrochemical workstation Voltalab 50 by cyclic voltammetry. Cyclic voltammetry was made in range <0;1100> mV with scan rate 25 mV s^{-1}. Measurements were done with 10 mmol l^{-1} $CdCl_2$, which was added to 10 ml 1 mol l^{-1} KCl.

4.3. Results and discussion

The output current response comparison of sensor type S1 and AC1 with gold working electrode is shown in figure 5. Sensor type S1 has 10x higher output current response than sensor type AC1.

The comparison of sensor type AC1 and S2 was made by heavy metal detection. Results are shown in figure 6 and figure 7. The sensors have gold working electrodes. Sensor type S2 has 10x higher output current response than sensor type AC1.

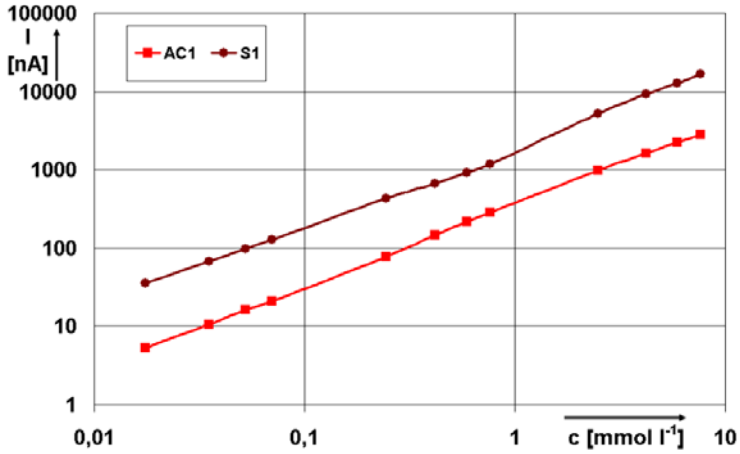


Fig. 5: The output current response comparison of sensor type S1 and AC1.

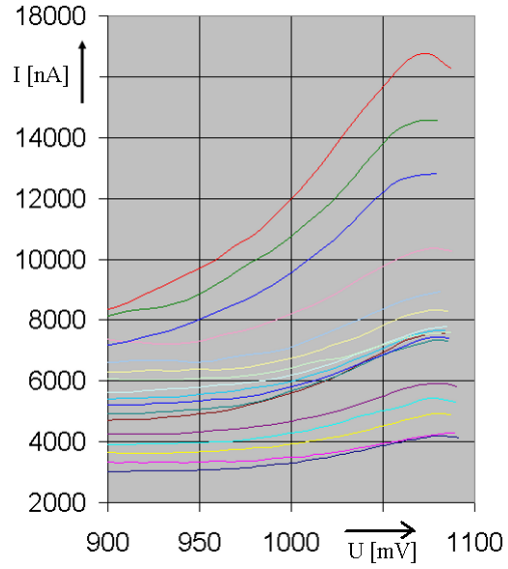


Fig.6: Cadmium detection by sensor type AC1.

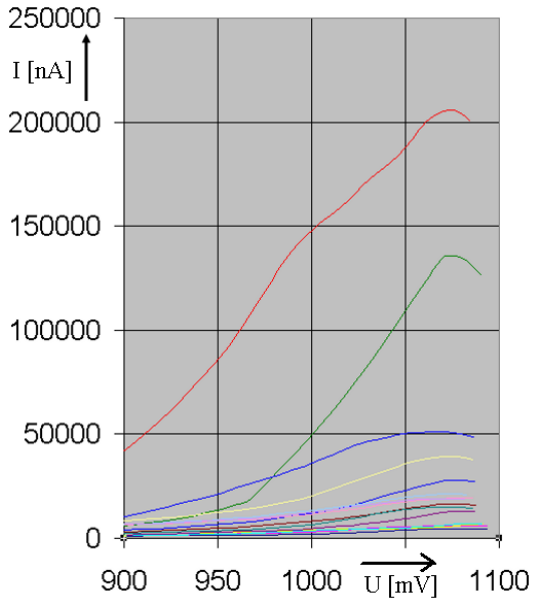


Fig. 7: Cadmium detection by sensor type S2.

5. CONCLUSIONS

The electrode system topology is very important problem in thick-film sensor design. One method of working electrode area increasing on small sensor substrate with maintenance of sufficient rate between working electrode area size : reference electrode area size is possible to be made by TFT paste elevations on basic electrode surface and optimization of topology. Our new redesigned and optimized sensors were compared with commercial one using the detection of product of some biosensors (H_2O_2) in case of sensor type S1 and the heavy metal detection ($CdCl_2$) in case of sensor type S2. In case of comparison of sensor S1 with commercial sensor AC1 it was found that our new sensor had 10x higher output current response than the commercial one. From the comparison of sensors type AC1 and S2 is clear that our new redesigned and optimized sensor S2 had also much higher output current response than the commercial sensor AC1.

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