Planar Electrode Topography Optimization for Electrochemical Sensor

Jan Prasek, Martin Adamek and Miroslav Cupal

Abstract – **This paper deals with the optimization of the planar three-electrode area of the thick-film electrochemical sensors for detection of species in water solutions. The aim of this work was to determine how the geometrical size and shape of the electrodes affect the output current response of the sensor. Various geometrically sized electrodes and shapes were designed, fabricated and compared using standard electrochemical solution of potassium ferro-ferricyanide. Finally, the current responses and wave potentials was evaluated and compared.**

Keywords – **Planar electrode, Thick-film sensor, Thick-film electrode, Electrochemical analysis, Electrode system**

I. INTRODUCTION

Monitoring of environment is nowadays trend. This monitoring is usually done using complex laboratory techniques. Voltammetry as an electrochemical analytical method is one of the methods used for detection of species in aqueous solutions. In many laboratories this method is performed using standard solid electrodes that substituted formerly used mercury drop electrodes [1] due to their toxicity in last few years. The advantage of solid electrodes is in the knowledge of their behavior in the solution which is well defined in literature, e.g. [2, 3]. The disadvantage of the standard electrodes is in their robustness which predestinates them to be unsuitable for on field analysis. Therefore the miniaturized voltammetric analytical devices are needed. These devices usually use miniaturized planar electrodes system forming up the sensor.

The miniaturized planar solid electrode systems (sensors) could be fabricated using several methods. One of them is thick film technology (TFT) [4, 5] which was primarily used for fabrication of hybrid circuits. With the improvement of surface mount technology in the end of 1980s, the TFT started to be used for special unconventional application which opened wide possibilities in creation of sensors, biosensors, displays, heater elements, etc. The advantage of TFT is a variability of used materials, low-cost production, flexibility, accessibility, non-vacuum and ecological friendly fabrication process, good reproducibility, etc.

J. Prasek is from the Department of Microelectronics, Faculty of electrical engineering and communication, Brno University of Technology, Udolni 53, 60200 Brno Czech Republic, e-mail: prasek@feec.vutbr.cz

M. Adamek is from the Department of Microelectronics, Faculty of electrical engineering and communication, Brno University of Technology, Udolni 53, 60200 Brno Czech Republic, e-mail: adamek@feec.vutbr.cz

M. Cupal has finished his master's degree study at the Department of Microelectronics, Faculty of electrical engineering and communication, Brno University of Technology, Udolni 53, 60200 Brno Czech Republic, e-mail: cmirek@centrum.cz

The problem of miniaturized planar electrode systems is in their unknown behavior in the solution. There are many producers offering small sensors (e.g. [6-8]). They present that their sensors have been used in many applications, but nobody of them ever presented any information about the sensor topology design and its influence to output current response or its behavior in the solution.

The aim of this work was to determine how the geometrical size and shape of the electrodes affect the output current response of the TFT electrochemical three-electrode sensor.

II. PLANAR SENSORS DESIGN AND FABRICATION

In this work there were done two different experiments. First of them was the investigation of sensor output current response with the change of geometrical electrodes areas, the second with the change of sensor electrodes shape with the fixed geometrical area of all three electrodes. Therefore it was necessary to design two different sets of electrodes as is mention below.

A. Sensors Design

The design of new three-electrode systems for both above mentioned experiments came out from the standard planar voltammetric electrochemical three-electrode thick-film sensor topography commonly used in our laboratory. The standard TFT voltammetric sensor topography used in our laboratory is shown in the figure 1. For both experiments the same sized alumina substrate (25.4×7.2 mm) and the same size of planar electrodes area (7×7 mm) were used for sensors design in this work.

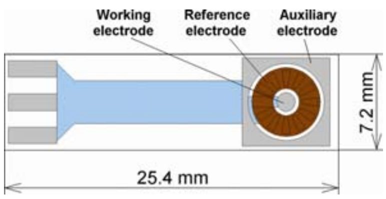

Fig. 1. Standard TFT voltammetric sensor topography [9]

For the first experiment seven different sensors with strip electrodes were designed. Generally it would be better to design more than seven variants of electrode areas. Unfortunately we were limited by one substrate with the size 2”×2” for both experiments because we had just one set of screens. All designed sensors are shown in the figure 2. The working electrode (WE) was designed with a fixed geometrical electrode area because the response is given mainly by the size of the electrode as it is given by the Cottrell equation [2, 3]. The designed size of auxiliary (AE) and reference (RE) electrodes are summarized in the table 1.

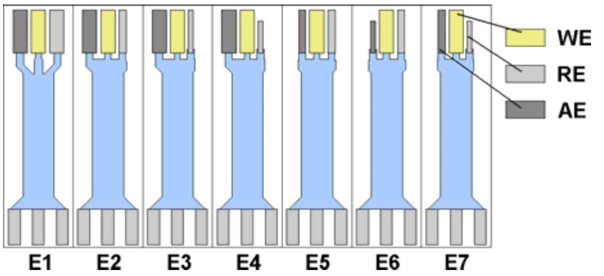

Fig. 2. Designed strip electrodes for the first experiment

TABLE 1. DESIGNED ELECTRODE AREAS FOR THE FIRST EXPERIMENT

	Electrode area [mm^2]						
	E1	E2	E3	E4	E5	E6	E7
WE	6,75	6,75	6,75	6,75	6,75	6,75	6,75
AE	6,75	6,75	6,75	6,75	3,375	1,69	3,375
RE	6,75	3,375	2,25	1,69	3,375	3,375	1,69

For the second experiment seven sensors with different shape of electrodes and the same geometrical electrodes area sizes were designed. According our previous experiments [10] the area of working and auxiliary electrode was designed to be 9 mm^2 and the area of reference electrode was designed to be 3 mm^2. All designed sensors are shown in the figure 3.

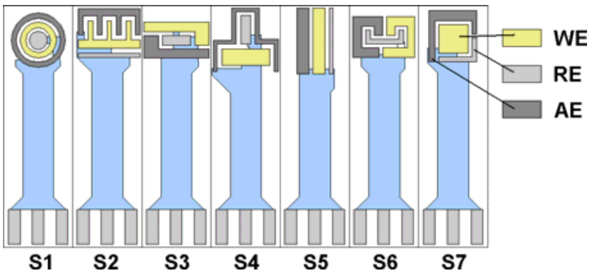

Fig. 3. Designed sensors for the second experiment

B. Sensors Fabrication

All TFT sensors were fabricated using standard screen-printing techniques on the alumina substrate. The conductive layer was fabricated from AgPdPt based paste

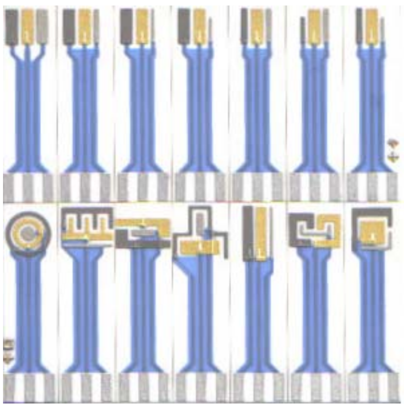

Fig. 4. Real sample of fabricated electrodes on one alumina substrate

(ESL 9562-G). The protecting layer was fabricated from dielectric paste (ESL 4917). Working electrodes were fabricated using Au based paste (ESL 8844-G) and auxiliary electrode using Pt based paste (ESL 5545). All these cermet pastes were obtained from ESL ElectroScience, UK and fired at 850 °C as recommended. Finally the reference electrodes were screen-printed using commercial special polymer AgCl pastes from DuPont Company (DuPont 5874 Ag:AgCl ratio is 65:35), and dried at 120 °C for 10 minutes. Substrate with deposited sensors is shown in the figure 4. There were fabricated five sets of electrodes and used for measurements.

III. EXPERIMENTAL

A. Chemicals

Solution of a 0.01 mol/L potassium ferrocyanide $K_4Fe(CN_6)$, 0.01 mol/L potassium ferricyanide $K_3Fe(CN_6)$ in 0.04 mol/L KOH was prepared using 18MΩ redistilled and deionized water (taken from Direct-Q Water Purification System, Millipore). All of used chemicals were purchased from Sigma Aldrich (St. Louis, USA).

B. Experimental method

All the measurements were done using potentiostat Voltalab PST050 (Radiometer analytical, Denmark). The measurement setup and response evaluation were done using a standard personal computer with VoltaMaster 4 control and evaluation software provided with the potentiostat. The experimental method used for measurement was cyclic voltammetry (CV) in range of the potential from -200 to 700 mV. The scan rate was set to 7 mV/sec. All experiments were done in a 10 ml voltammetric cell (25 °C) using a three-electrode system on the measured sensors. The obtained anodic current and wave potentials were red for evaluation.

IV. RESULTS AND DISCUSSION

In this work there were done two different experiments. Results from both experiments are shown and discussed in next two subsections.

A. Experiment 1: Influence of the Size of Electrodes

First experiment was devoted to the influence investigation of geometrical size of reference and auxiliary electrodes change to the sensor anodic output current response and wave potential. The real sizes of the fabricated electrodes almost corresponded with the designed ones, so the designed values shown in the table 1 were used for evaluation. In this case there were measured five samples of each sensor and the resulting values were averaged from all measurements.

Reference electrode experiments

For this experiment the sensors E1, E2, E3 and E4 from the figure 2 were used. The designed sizes of the electrodes are shown in the table 1.

The influence of reference electrode size to output current response and wave potential is shown in the figure 5 and 6 respectively. From the figure 5 is clear that the sensitivity decrease with the size of the electrode (obtained sensitivity is -0.15 μA/mm^2). It is in contradiction with the results obtained in previous measurements [10] with standard electrodes where the gradient was positive. Figure 6 shows that there is almost no dependence of wave potential on the size of RE.

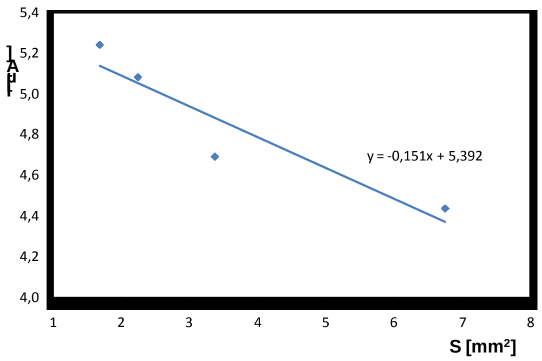

Fig. 5. Dependence of output current response on the size of RE (size of WE and AE were on fixed value)

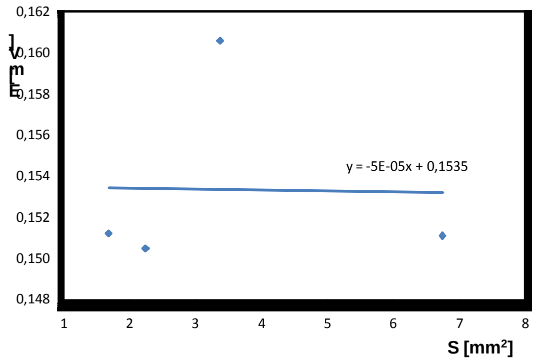

Fig. 6. Dependence of wave potential on the size of RE (size of WE and AE were on fixed value)

Auxiliary electrode experiments

For this experiment the sensors E4 and E7 from the figure 2 were used. The designed sizes of the electrodes are shown in the table 1.

The influence of auxiliary electrode size to output current response and wave potential is shown in the figure 7 and 8 respectively. From the results show in the figure 7 is clear that the current response is increasing with the size of the auxiliary electrode area. The sensitivity obtained is 0.32 μA/mm^2. Probably this behavior is given by the current density between WE and AE. It could be expected that with next increment of the AE size, the current will be stabilized at a fixed value. The change of wave potential shown in the figure 8 is insignificant because the sensitivity is -17 μV/mm^2 only.

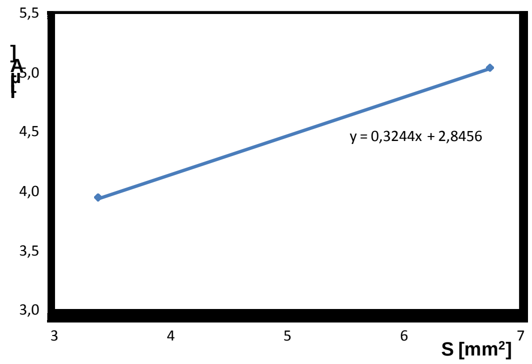

Fig. 7. Dependence of output current response on the size of AE (size of WE and RE were on fixed value)

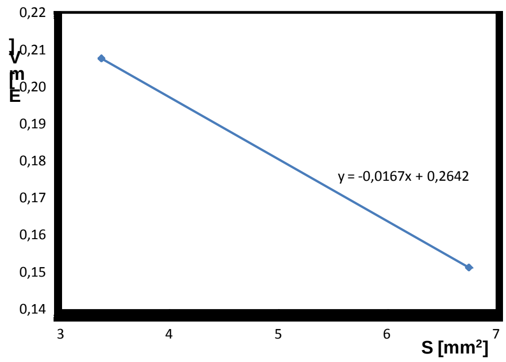

Fig. 8. Dependence of output current response on the size of AE (size of WE and RE were on fixed value)

B. Experiment 2: Influence of the Electrode Area Shape

Second experiment was devoted to the influence investigation of sensor electrode area shape with the fixed geometrical size of all three electrodes to the sensor anodic output current response and wave potential. In this case there were measured five samples of each sensor. Obtained results for all sensors are shown in the figure 9 and 10.

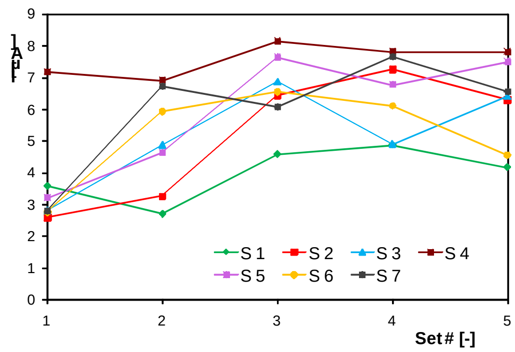

Fig. 9. Dependence of output current response on the shape of the sensor electrode area

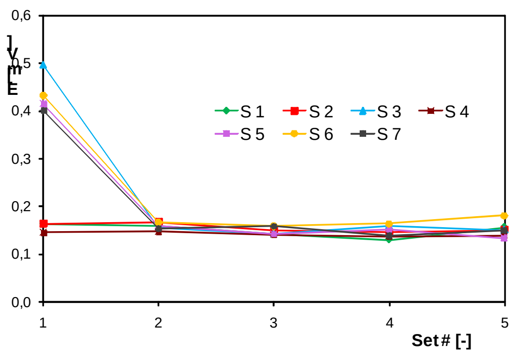

Fig. 10. Dependence of wave potential on the shape of the sensor electrode area

From the results shown in the figure 9 and 10 is clear that the highest current response and reproducibility was achieved with the sensor number S4. The lowest response with a relative good reproducibility was achieved with the sensor S1 that represents commonly used rounded shape of the electrode area. Considering some kind of error for the first set of electrodes, the change of half wave potential was negligible. The most reproducible results were achieved with the sensor S4 and S6 in this case.

V. CONCLUSIONS

There was investigated the optimization of planar electrode system of thick-film planar electrochemical sensor in this work. There were done two different experiments.

First experiment was devoted to the influence investigation of geometrical size of reference and auxiliary electrodes to the sensor anodic output current response and wave potential. For this purpose, seven different sensors were designed and fabricated. It was found that the dependence of output current response with the change of RE area size had negative gradient in comparison with our previous results. The current response dependence with the change of AE area size was increasing. The size of AE was probably chosen badly and it needs to be measured in wider range of AE area sizes in the next experiments, but it could be expected that with next increment of the AE size, the current will be stabilized at a fixed value due to maximum current density passing through WE. The influences of RE and AE areas sizes to anodic wave potential was almost negligible in both cases.

The second experiment was devoted to the influence investigation of sensor electrode area shape with the fixed geometrical area size of all three electrodes to the sensor anodic output current response and wave potential. For this purpose, seven different sensors were designed and fabricated. The highest current response and reproducibility was achieved with the sensor number S4. The lowest current response with a relative good reproducibility was achieved with the sensor S1 that represents commonly used rounded shape of the electrode area. Considering some kind of error for the first set of electrodes, the change of half wave potential was almost independent on the shape of electrode area.

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