

THICK-FILM ELECTROCHEMICAL SENSOR WITH DEPOSITED CARBON NANOTUBES

**Jan Prasek¹, Martin Adamek¹, Jaromir Hubalek¹,
Ondrej Jasek², Lenka Zajickova²**

¹ Dept. of Microelectronics, Brno University of Technology, Udolni 53, 602 00 Brno, Czech Republic, phone: +420 541 146 136, email: prasek@feec.vutbr.cz

² Dept. of Physical Electronics, Masaryk University, Kotlarska 2, 602 00 Brno, Czech Republic

This paper deals with new possibilities of thick-film electrochemical sensor working electrode fabrication. The working electrode of common electrochemical sensor was modified with nanostructured layer made of vertically aligned carbon nanotubes. Carbon nanotubes were grown directly on working electrode substrate. The aim was to create homogenous and high density carbon nanotubes layer directly on the thick-film Ag substrate layer. Working electrodes modified with carbon nanotubes were tested against classical Ag/AgCl electrode using sample solution containing heavy metals ions. We were able to detect cadmium ions in the concentration in units of $\mu\text{mol/L}$.

Keywords: thick-film sensor, carbon nanotubes, cadmium analysis

1. INTRODUCTION

Trace determination of species in living environment is very important in many areas. One group of the species is the group of heavy metals. Heavy metals are very toxic for human life and therefore they need to be monitored in environment and food industry. Heavy metals can be easily determined by polarography with mercury drop electrode (J. Heyrovsky, 1922). New trend in fast heavy metal determination is focused on using solid electrodes. Substitution of mercury drop electrode is still aim of science since 1950's [1, 2]. In last years, graphite electrodes start to be used in the heavy metal analysis, e.g. thick-film graphite electrodes were used for mercury determination with the stripping voltammetry [3].

Nowadays carbon nanotubes are in the centre of investigation as very perspective solid electrodes. Oxidized multiwall carbon nanotubes (MWCNTs) were used as a novel adsorbent for removing Ni(II) from aqueous solution [4]. The metal adsorbance of the carbon nanotubes makes them very promising in heavy metal determination.

The way as these solid electrodes can be prepared is using the thick-film technology (TFT) which enables also low-cost small sensor fabrication. In past the TFT was utilized for production of hybrid integrated circuits [5], later was used for fabrication of special integrated circuits, small series of nonstandard integrated circuits and prototypes [6]. The advantage of TFT sensors are low dimensions, good reproducibility, mechanical and electrical properties of electrodes and well accessible and ecological fabrication process [7].

The significant advantage is low cost of the electrodes (e.g. platinum electrode containing 1 mg of Pt) which enables to use the electrodes only for few numbers of analyses and high variability of used materials. Because of high mechanical resistance of thick films fabricated from cermets pastes the several deposition methods of sensing materials, including high temperature processes, can be used for the working electrode formation. It predestinates the CNTs exploitation as sensing material on the electrode [8]. The CNTs belong to the most promising nano-materials, they show unique electronic, mechanical and chemical properties [9] that lead to many several applications. They can be prepared by arc discharge [8], laser ablation [10] and chemical vapor deposition [11] methods. For industrial applications it is desirable to produce vertically aligned CNT films with uniform properties. The aim of this work is to prepare the sensors with carbon nanotubes grown directly on sensor's electrode using synthesis of the vertically aligned CNTs in atmospheric microwave plasma torch discharge and to find out the possibility of its use in field of electrochemical analysis. For this purpose a special TFT sensor was designed which is suitable for the working electrode material varying with eventual possibility of different electrochemical systems utilization.

2. EXPERIMENTAL

2.1 Sensor design

As a sensor on alumina for electrode material properties measurement the thick-film electrodes were designed and published (fig. 1) [12]. An Ag based paste has been designed for leads and connector. The reference electrode material has been designed also based on Ag that can be electrochemically covered by AgCl layer [13] after the main sensor fabrication process. Auxiliary electrode material is suggested from a Pt paste but the material of each electrode can be changed by a use of other type of the paste. The nanopatterned working electrodes preparation is objective of the work to be described below.

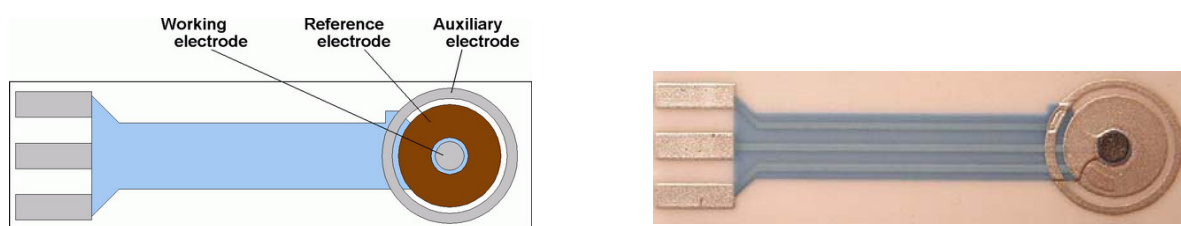


Fig. 1 Standard TFT sensor design (left) and its real sample (right) [12].

The substrate with electrode topology have been designed to be compatible with electrochemical analytical devices – Micro Flow System from BVT Technology and Rotating Vessel [14, 15] that are commonly used in our laboratory to ensure the reproducible conditions during the measurement under flowing electrolyte.

2.2 Sensor fabrication

The TFT sensor was fabricated using screen-printing techniques. The TFT material used for auxiliary electrode, reference electrode and conductive layer was

ESL 9912-D paste and for dielectric layer ESL 4913-G paste. For the working electrode the ESL 4913-G paste (Ag) and ESL 8844-G paste (Au) were used (all pastes were ESL ElectroScience, USA).

2.3 Working Electrode Preparation

The nanopatterned working electrode on special designed electrode substrate (fig. 2) is created in several steps. The bottom layer of the working electrode is formed from the Ag paste. The carbon nanotubes grow vertically aligned on the working electrode surface forming nanopatterned structure. This electrode modification by the nanotubes is homogeneous and the electrode surface is completely covered with high density amount of the nanotubes. To deposit the carbon nanotubes on the working electrode its surface was modified by thin nickel layer (10-20 nm) created by magnetron sputtering or by thermal vacuum evaporation served as a catalyst in the CNTs growth and argon, hydrogen and methane were used as working gases. The gas flow rates were controlled by electronic flow controllers. Microwave power of 400 W (2.45 GHz, 2 kW max. power) is supplied by a microwave generator and transmitted by a waveguide through a coaxial line to a hollow nozzle electrode. A ferrite circulator protects the generator against the reflected power by rerouting it to the water load. The coaxial line and the electrode accommodated a dual gas flow. Argon (1500 sccm) flew through a central opening (1 mm) and the deposition mixture, H_2/CH_4 (42/430 sccm), was added by a set of holes in the outer housing. The plasma expands from the central nozzle forming a torch discharge. A quartz tube, 40mm in outer diameter, separates the discharge from surrounding atmosphere. At the bottom it is sealed by a Teflon piece to the flange of the outer coaxial conductor. At the top it is closed by an upper flange with an exhaust tube and a sealed feed through for a substrate holder. The substrate holder is another quartz tube, 18 millimeters outer diameter, fixed at the upper flange. This tube is closed at its top by a quartz window. At the opposite side, i.e. close to the discharge nozzle, two slits are cut through the tube. The sensor was facing the torch during the deposition. Its temperature was measured by Raytek Thermalert TX pyrometer from the back side. After the plasma torch was ignited by an auxiliary rod electrode in flowing argon, the sensor was placed at the desired deposition distance (30-50 mm) from the nozzle and the deposition mixture H_2/CH_4 was added. The deposition temperature (T_d) was regulated by the deposition distance and it was varied from 950 to 1100 K. The deposition time (t_d) was 1 to 15 minutes. The more detailed description of the experimental setup and deposition procedure can be found in [16].



Fig. 2 Working electrode substrate design (left) and its real sample (right).

2.4 SEM analysis

Surface morphology of the deposits was studied by a scanning electron microscopy (SEM) with JEOL 6700F microscope equipped with an EDX analyzer. The acceleration voltage was usually 5 kV and working distance was in the range of 8-9 mm. The pictures were taken at several points from the surface of the working electrode.

2.5 Chemicals

All measurements were carried out in the 1 mol/L potassium chloride buffer prepared from potassium chloride (PENTA, CZ) with p.a. grade purity added to water ACS reagent (Sigma-Aldrich). As a heavy metal sample the 0.01 mol/L cadmium chloride (ML chemica) with p.a. grade purity in water ACS reagent was used. All the chemicals were used as received.

2.6 Experimental method

Differential pulse voltammetry (DPV) in range of the potential from -1.1 V to 0 with scan rate of 10 mV/sec was performed using the Polarographic analyzer PA4 device (Laboratorni pristroje Prague, Czech Republic). Amplitude of the pulse was 50 mV with pulse length of 100 ms and pulses distance also 100 ms. The PA4 device was connected to a personal computer through A/D converter.

Electrochemical experiments were carried out in a 10 mL voltammetric cell, at room temperature (25°C), using a two-electrode configuration system using a common Ag/AgCl (Cyrus, Czech Republic) reference electrode. An oxygen elimination was ensured using a buffer solution with N₂ bubbling through.

3. RESULTS AND DISCUSSION

The carbon nanotubes were successfully deposited on the Ag paste based working electrode with a Ni catalyst. The catalyst layer (10 nm of Ni) was vacuum evaporated on the top of the sensor working electrode. The electrode material selection will influence the electrode surface morphology and the nanotubes growth. This issue was confirmed by SEM analysis of the carbon nanotubes deposits. The surface roughness and interactions between the paste and nickel catalyst are responsible for different growth results. The surface of the Ag based paste is rough because of large crystals. Therefore the CNTs deposit has got small inhomogeneities in growth (fig. 3a, 3b). There are clumps of the nanotubes more or less large with interspaces not covered with nanostructures. These interspaces have to originate from absence of the catalyst whose active properties disappeared in interactions with the electrode surface during high temperature process and large crystals causing significant surface roughness. In addition the binder of the crystal particles cover them at thick film producing large intercrystal spaces. Homogenously covered parts of the electrode form large area of nanoelectrodes huge increasing of the surface (see fig. 3c).

Fabricated sensor was tested for determination of cadmium(II) ions concentration because of cadmium have been shown as trace of heavy metal ion that can be detected [17,18]. The measurements were performed using differential pulse voltammetry in the 1 mol/L of KCl buffer at scan rate of the 10 mV/s. Output current

DPV response has been measured under several additions of the 10 mmol/L CdCl_2 into the buffer. The responses to concentrations of the 110 and 220 $\mu\text{mol/L}$ are shown in the fig. 4. The peaks determine cadmium ions oxidation which was monitored on the working electrode. High level of the response shows and confirms CNTs suitability for the cadmium detection. The light ends of the nanostructures, as all pictures in fig. 3 show, are rest of the catalyst layer. It is difficult to remove them but fortunately the catalyst has not influenced the sensor response.

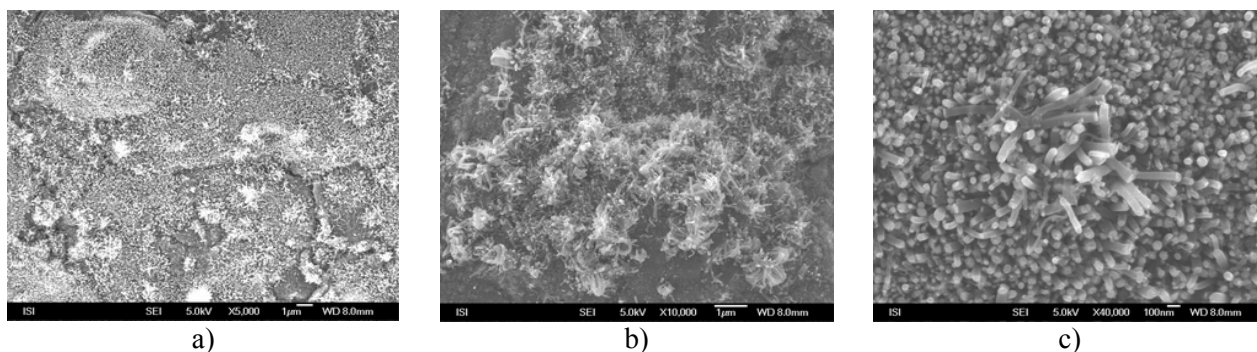


Fig. 3 SEM micrographs of the working electrode with the carbon nanotubes deposited on the Ag layer.

The detection limit was determined at level of the 5 $\mu\text{mol/L}$ of the cadmium ions. The slope of calibration curve expressing the sensitivity of the sensor has been determined the 0.089 $\mu\text{A.L}/\mu\text{mol}$. These results are comparable with the others carbon based material deposited on the working electrode. If inhomogeneities in the CNTs layer and less sensitive oxidizing reaction are considered the CNTs vertically aligned on the electrode is perspective material and method for the nanopatterned working electrode formation.

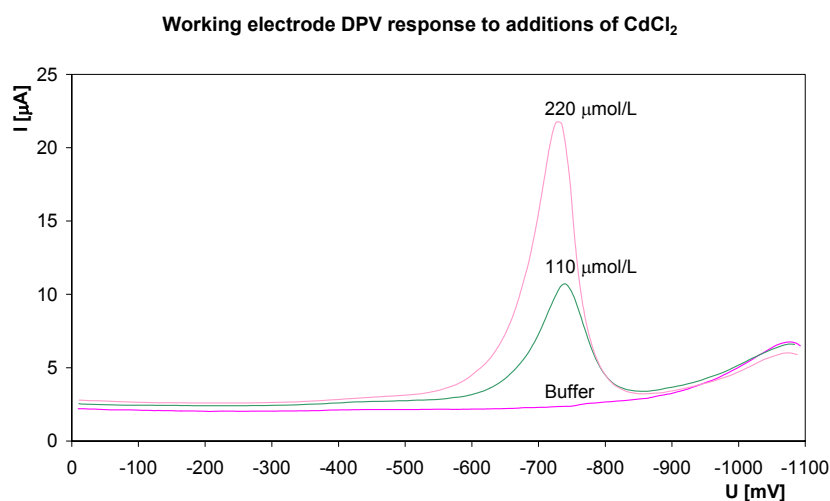


Fig. 4 The current response to two different concentration of cadmium ions.

4. CONCLUSIONS

First sample of the sensor with vertically aligned carbon nanotubes formed on the working electrode surface was prepared and tested in this work. The nanotubes grow homogeneously on the surface but inhomogeneities as open areas without the nanotubes were found. The issue is caused by roughness of the electrode surface and insufficient elimination of the intermetallic reactions of the catalyst layer with the electrode surface. In addition the results show that residues of nickel catalyst from CNTs growing process do not influence the sensor response because of missing any other peaks in the responses. The results have shown us that the sensor is able to detect the concentrations of 5 $\mu\text{mol/L}$ of the cadmium ions. This outcome is significant for the CNTs and method utilization on the nanopatterned working electrode creation if the quality of the nanotubes homogeneity on the first sample is considered.

5. ACKNOWLEDGEMENT

Funding for this work was provided by the Czech academy grant agency under the contract GAAV 1QS201710508, Czech grant agency under the contract GACR 202/05/0607, GACR 102/06/1624 and Czech Ministry of Education in the frame of Research Plan MSM 0021630503 MIKROSYN.

6. REFERENCES

- [1] Rogers, L. and Lord, S., *Analytical Chemistry* 24 (3), 596-596, 1952.
- [2] Delimarskii, Y. and Gorodyskii, A., *Industrial Laboratory* 28 (9), 1103-1109, 1962.
- [3] Stojko, N.Y., Brainina, K.Z., Faller C., et al., *Analytica Chimica Acta* 371 (2-3), 145-153, 1998.
- [4] Chen, C. and Wang, X., *Industrial & Engineering Chemistry Research* 45 (26), 9144-9149, 2006.
- [5] Haskard, M. and Pitt, K. *Thick-film Technology and Application*, Elektrochem. Pub. LTD, GB 1997.
- [6] Hascard, M. *Thick-film Hybrids Manufacture and Design*, Prentice Hall, 1988.
- [7] Harsányi, G. *Polymer Films in Sensor Applications*, Technomic Publishing Co., Lancaster (USA), Basel, 1995. p. 435.
- [8] Iijima, S. *Nature* 354 – 1991, 56.
- [9] Ajayan, P. M. *Nanotubes from carbon*, *Chem. Rev.* 99 – (1999) 1787.
- [10] Thess, A., Lee, R., Nikolaev, et al. *Science* 273 (1996) 483.
- [11] Lee, Ch.J., Kim, D.W., Lee, T.J., et al. *Chem. Phys. Lett.* 312 (1999) 61.
- [12] Prasek, J., and Adamek, M., *IEEE Sensors 2004 proc. IEEE Sensors 2004*. Vienna, Austria: IEEE, TU Wien, 2004, pp. 749 - 752.
- [13] Lanz, M., Schürch, D., and Calzaferri, G. *Journal of Photochemistry and Photobiology A: Chemistry* 120 (1999) 105-117, Elsevier.
- [14] Prasek, J., Adamek, M., Hubalek, J., Adam, V., Trnkova, L. and Kizek, R., *Sensors* 2006, 6, ISSN 1424-8220, 2006, 11, pp. 1498 - 1 512.
- [15] Babula, P., et al., *Sensors*, 2006, 6, p. 1466 - 1 482.
- [16] Zajickova, L., Elias, M., Jasek, O., Kudrle, V., Frgala, Z., Matejkova, J., Bursik, J., Kadlecikova, M. *Plasma Phys. Control. Fusion* 47 (2005) B655.
- [17] Gao, X., Wei, W., Yang, L. and Guo, M., *Electroanalysis* 18 (5), 485-492, 2006.
- [18] Liu, G., Lin, Y., Tu, Y. and Ren Z., *Analyst* 130 (7), 1098-1101, 2005.