07 - 10 September 2009

PROCEEDINGS

54. IWK

Internationales Wissenschaftliches Kolloquium
International Scientific Colloquium

Information Technology and Electrical Engineering - Devices and Systems, Materials and Technologies for the Future

Faculty of Electrical Engineering and Information Technology

Startseite / Index:
http://www.db-thueringen.de/servlets/DocumentServlet?id=14089

TECHNISCHE UNIVERSITÄT
ILMENAU

Impressum

Herausgeber: Der Rektor der Technischen Universität Ilmenau
Univ.-Prof. Dr. rer. nat. habil. Dr. h. c. Prof. h. c.
Peter Scharff

Redaktion: Referat Marketing
Andrea Schneider

Fakultät für Elektrotechnik und Informationstechnik
Univ.-Prof. Dr.-Ing. Frank Berger

Redaktionsschluss: 17. August 2009

Technische Realisierung (USB-Flash-Ausgabe):
Institut für Medientechnik an der TU Ilmenau
Dipl.-Ing. Christian Weigel
Dipl.-Ing. Helge Drumm

Technische Realisierung (Online-Ausgabe):
Universitätsbibliothek Ilmenau
ilmedia
Postfach 10 05 65
98684 Ilmenau

Verlag:
Verlag ISLE, Betriebsstätte des ISLE e.V.
Werner-von-Siemens-Str. 16
98693 Ilmenau

ISBN (USB-Flash-Ausgabe): 978-3-938843-45-1
ISBN (Druckausgabe der Kurzfassungen): 978-3-938843-44-4

Startseite / Index:
http://www.db-thueringen.de/servlets/DocumentServlet?id=14089

DETERMINATION OF ZN, CD, PB BY BISMUTH-COATED MICROELECTRODE ARRAY BASED ON DIAMOND-LIKE CARBON THIN FILMS

M. Varga[1], M. Vojs[1], V. Rehacek[1], M. Vesely[1], M. Michalka[2]

[1]Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Department of Microelectronics, Ilkovičova 3, 812 19 Bratislava, Slovak Republic
[2]International Laser Center, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

ABSTRACT

Diamond-like carbon (DLC) thin films deposited by unfiltered cathodic pulsed arc in vacuum system with high sp^3 content are more promising electrode material than conventional carbon-based electrodes, because they have wide potential window and low background current.

The determination of trace heavy metals such as lead, cadmium and zinc, by anodic stripping voltammetry (ASV) on microelectrode array in environmental analysis is very attractive due to its remarkable sensitivity, extremely low detection limits (< ppb), portability and ease to application.

General trend for more environmentally-friendly analytical methods is bismuth film electrode as bismuth has low toxicity analytical characteristics in comparison with mercury, it can lead to widely spread use of these devices.

Key words - DLC, BiFE, MEA, SWASV, trace heavy metals

1. INTRODUCTION

Glassy carbon, carbon paste, graphite and other metal films have been reported as support materials for electrochemical analysis [1]. Nano-crystalline diamond and diamond like carbon (DLC), as relative new materials in this field, can open wide range of applications for their excellent mechanical properties, chemical inertness to any acids, alkaline solutions or organic solvents. Simultaneously, the use of mercury is in many countries denied, as a consequence this causes a drop-out of important segment in electrochemical industry. For this reason the basic research in finding suitable electrodes using non-mercury active materials is forced. Bismuth has a potential to replace toxic mercury used most frequently for determination of heavy metals by square-wave anodic stripping voltammetry (SWASV) [2], [3]. Analytical performance of the bismuth film electrode (BiFE) on DLC films is influenced by its properties.

In this paper we describe a study of Zn, Cd, Pb trace metal determination by bismuth in situ coated microelectrode array (MEA) based on diamond-like carbon thin films characterized by anodic stripping voltammetry.

2. EXPERIMENT

DLC films with different deposition conditions were prepared by unfiltered cathodic arc in vacuum system on highly conductive (0.008 - 0.024 Ωcm) Si (100) substrates. The area which acts as working electrode (array of 50,625 microdiscs with 3 μm in diameter and distance of 20 μm between microdiscs) is shown on Fig. 1. Process of MEA definition was by standard photolithographic process which is decribed in details elsewhere [4].

Before the deposition substrates were ultrasonically cleaned for 10 min in izoprophylalcohol bath. DLC deposition process could be characterized in tree steps: the first step was chamber pumping down to $p_0 = 3x10^{-3}$ Pa, the second step was substrate cleaning by 10 min Ar ion bombardment (60 sccm, p = 0.2 Pa) and the last step was carbon layer deposition. Through the deposition, gas flows into reaction chamber were controled (Ar, N_2 in 0, 30, 50 and 70 sccm), applying 5 000 pulses with 5 Hz repeatability.

The morphology and composition of MEA has been analyzed by Raman spectroscopy and scanning electron microscopy (SEM). All solutions were prepared from analytical grade chemicals in 18 MΩ.cm deionized water. A three-electrode arrangement was used in all experiments. As reference electrode the home-made Ag/AgCl/agar Cl^- (3 mol/L)/agar NO_3^- (1 mol/L) electrode was used and as the counter electrode a platinum wire served. Voltammetric experiments were performed with an electrochemical sensor interface (PalmSens, Palm Instruments BV) in combination with a personal computer.

3. RESULTS AND DISCUSION

Layers after deposition have continual and adherent character with the thickness from 81 nm (DLC) to 206 nm (Ar = 70 sccm, N_2 = 70 sccm), which was dependent on pressure in the chamber. In Fig. 2 the dependence of growth rate on pressure is given. With increasing pressure the growth rate has

increased from 4.9 nm/min for DLC to 12.4 nm/min for carbon nitride (CN_x, 70/70 sccm Ar/N_2).

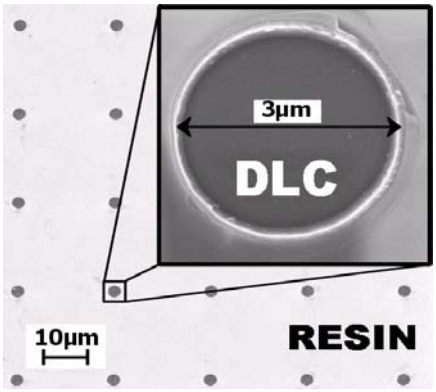

Fig. 1 Detail of the microelectrode array

Fig. 3 shows a comparison of DLC and CN_x film Raman spectra. With increasing thickness an intensity decrease of sharp peaks for Si (520 cm^{-1}), and Si compound (960 cm^{-1}) occurs. Characteristic for these spectra is the transformation intensity of "D" and "G" broad band dependence on working gas pressure. This change is corresponding to activation of disordered bonds of carbon in films [5]. Further growth of C-N bonds is corresponding to existing "L" band around 720 cm^{-1}. In Fig. 4 different Raman spectra from DLC layers with argon gas (Ar = 30 sccm) during deposition are shown.

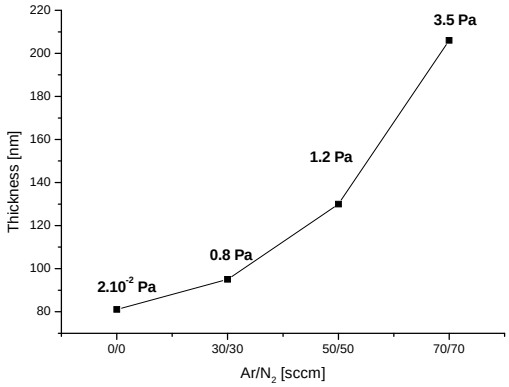

Fig. 2 Dependence of DLC and CN_x film thickness on gas flow

The electrode behavior was characterized by cyclic voltammetry in 0.1 mol/L KNO_3 buffer (pH = 2) with 0.5 mg/L Bi^{3+}. Pre-concentration time was 180 s at a potential of -1.3 V. After 15 s in a potential range from -1.3 to -0.4 V at a scan rate of 50 mV/s effect of bismuth film was investigated. CV of bismuth peak for different gas flow is shown in Fig. 5. From these voltammograms the influence of deposition conditions is not clearly visible, but we choose DLC 0_0 and DLC 30_0 as an electrode material for heavy metal trace detection for better current response.

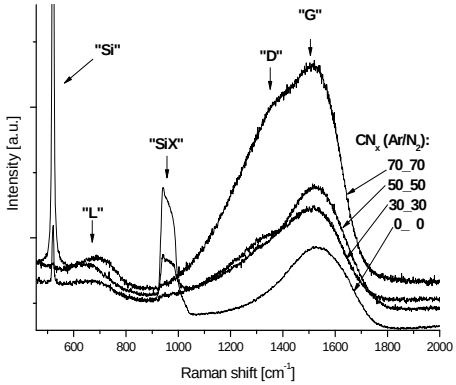

Fig. 3 Raman spectra of DLC and CN_x films

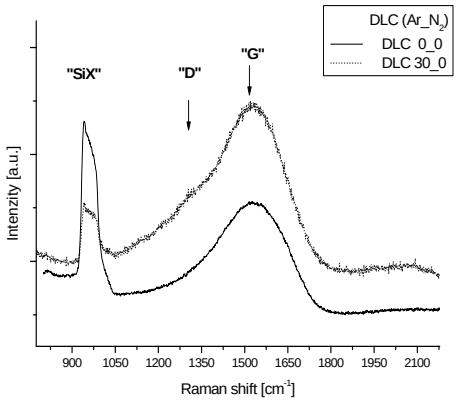

Fig. 4 Raman spectra of DLC films: DLC 0_0 (Ar = 0 sccm), DLC 30_0 (Ar = 30 sccm)

Bismuth-plated DLC microelectrode arrays for in situ determination of Pb^{2+}, Zn^{2+}, Cd^{2+} were prepared by co-deposition of Bi^{3+} and metals at −1 300 mV for 180 s versus Ag/AgCl/Cl^- in a plating solution of $Bi(NO_3)_3$ in a supporting electrolyte with a different content of heavy metals. Stripping currents from reoxidation of analyte were recorded by SWASV.

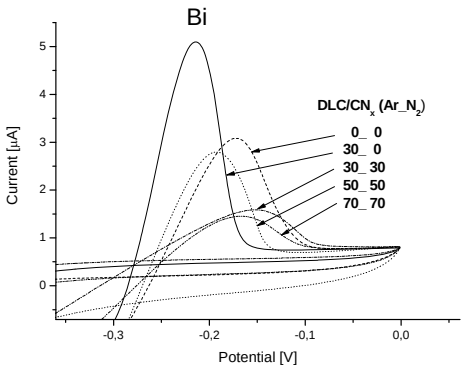

Fig. 5 Influence of pressure on bismuth film formation in 0.1 mol/L KNO_3 with 0.5 mg/L Bi^{3+}

The influence of many parameters, including concentration of plating solution, kind of supporting

electrolyte and concentration of heavy metal on the stripping current responses has been analyzed. Influence of concentration of a plating solution on bismuth film formation for in situ technique was investigated in range of 0.5 – 2 mg/L Bi^{3+} in 0.1 mol/L acidified KNO_3 (pH 2). For the SWASV experiments, concentration of 0.5 mg/L has been selected because a stripping current was not increased at higher than 1 mg/L concentration and bismuth peak shape was deformed moreover [6]. We estimated the optimal concentration of Bi^{3+} for measurement at 0.5 mg/L ($1x10^{-5}$ mol/L).

The dependencies of voltammetric response of bismuth-plated DLC array without Ar (DLC 0_0) and with Ar (DLC 30_0) on metal concentration are shown in Fig. 6 and Fig. 7, respectively. Stripping current was linear in the range from 2×10^{-8} to 8×10^{-8} mol/L concentration of metals complex at 180 s pre-concentration time. Sensitivity of trace heavy metals detection for DLC 0_0 was for Zn = 1.465; Cd = 0.775; Pb = 2.59 μAL/μmol and sensitivity for DLC 30_0 was for Zn = 1.12; Cd = 0.845; Pb = 1.62 μAL/μmol.

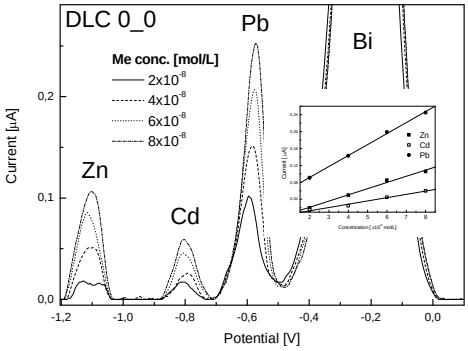

Fig. 6 Dependence of current responses of DLC 0_0 array; c(Bi^{3+}) = 1 x 10^{-5} mol/L on Zn^{2+}, Cd^{2+} and Pb^{2+} concentration 2 - 8x10^{-8} mol/L with calibration curve inside; pre-concentration time 180 s

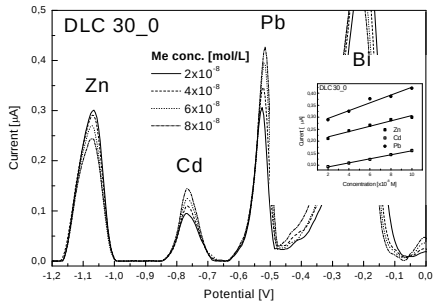

Fig. 7 Dependence of current responses of DLC 30_0 array; c(Bi^{3+}) = 1 x 10^{-5} mol/L, Zn^{2+}, Cd^{2+} and Pb^{2+} concentration 2 - 8x10^{-8} mol/L with calibration curve inside; pre-concentration time 180 s

4. CONCLUSIONS

Bismuth film microelectrodes have a potential to replace toxic mercury used most frequently for determination of heavy metals (Cd, Pb, Zn) by anodic stripping voltammetry. We have developed nitrogen doped diamond-like carbon microelectrode array consisting of 50,625 microdiscs with 3 μm in diameter and interelectrode distances of 20 μm as a support for bismuth electroplating on highly conductive silicon substrate. The properties of DLCs were analyzed by Raman spectroscopy, cyclic voltammetry and anodic striping voltammetry. The morphology of bismuth-coated DLCs has been investigated by scanning electron microscopy.

It was found that the analytical performance of bismuth film microelectrodes is influenced by the properties of DLCs. The influence of bismuth plating solution and supporting electrolyte on current responses has been investigated. We have found that the stripping current for bismuth-coated DLC array is linear in the range from 2×10^{-8} to 8×10^{-8} mol/L concentrations of heavy metals diluted in water. The stripping current responses of DLC 30_0 microelectrode array, reached under the same conditions, were lower in comparison with DLC 0_0 bismuth-coated array. Measured LOD did indicate a better detection of Zn^{2+} and Pb^{2+} (LOD_{Zn} = $0.9x10^{-8}$; LOD_{Pb} = $0.4x10^{-8}$ mol/l) for DLC 0_0 and Cd^{2+} (LOD_{Cd} = $0.5x10^{-8}$) for DLC 30_0, which is not corresponding to Bi^{3+} stripping on DLC/CN_x, where the current is approximately twice higher for DLC 30_0 than for DLC 0_0.

5. ACKNOWLEDGEMENT

This work was financially supported by grants of Slovak Research and Development Agency no. APVV-0548-07, LPP-0246-06 in Center of Excellence CENAMOST VVCE-0049-07, and Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences No. VEGA 1/0807/08, 1/0857/08.

6. REFERENCES

[1] A. Economou, Trends Anal. Chem. 24, pp. 334–340, 2005

[2] R. Feeney, S. Kounaves, Electroanal. 12, pp. 677–684, 2000.

[3] X. Xie, D. Stuben, Z. Berner, J. Albers, R. Hintsche, E. Jentzen, Sens.Actuator B 97, pp. 168–173, 2004.

[4] I. Svancara and K. Vytras, "Elektroanalyza s bismutovymi elektrodami", Chem. Listy 100, pp. 90-113, 2006.

[5] V. Rehacek et al., Sensors and Actuators B 127 pp. 193–197, 2007.

[6] Ferrari A.C., et al., In Journal of Non-Crystalline Solids 266-269, (2000), p. 765-768