HIGH STABILITY BISMUTH-FILM ELECTRODES FOR THE DETERMINATION OF TRACE METALS BY ANODIC STRIPPING VOLTAMMETRY

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1. Introduction

Detection of trace heavy metals in water is not a new topic, but there are several reasons for which this issue is brought to the forefront again. One of the most preferred reasons why we are dealing with trace heavy metals is the fact that it is necessary to replace existing mercury-film electrodes (MFE). However, because of mercury toxicity, future regulations and occupational health considerations may severely restrict the use of mercury. In search for alternative electrode materials, bismuth-film electrodes (BiFE) offer comparable performance to MFE for anodic stripping voltammetric measurements of trace metals, as it was shown. Stripping analysis has proved to be a powerful technique for the determination of trace heavy metals in various samples. Properties of bismuth films include simple preparation, high sensitivity, excellent peak resolution, negligible toxicity and ability to operate in highly alkaline media. Carbon substrates such as glassy carbon, carbon paste [1], carbon fiber, impreg-nated graphite [2], diamond-like carbon (DLC) [3], boron-doped diamond (BDD), carbon nanotubes [4], pyrolyzed photoresist [5], but also gold, platinum and others seems to be a good choice for measurement. In this paper we investigated properties of nanocrystaline diamond (NCD) as a substrate for in-situ bismuth electroplating electrode system. The composition of carbon has been analyzed by Raman spectroscopy.

2. Experiment

NCD films were produced in the double bias enhanced HF CVD reactor with sheet resistivity ~ 10 MQ/sq. As substrate highly conductive (0.008-0.024 Ω cm) N (100) type silicon substrate was used. Throughout the deposition, gas flows in reaction chamber were

controlled to be 300 sccm for H₂ and 3, 6, 9, 12, 15 sccm (corresponding to 1-5% percent of CH₄ in H₂). The total pressure in the reactor was 3 000 Pa. Deposition process was divided into two steps: the first step was 40 min seeding with nano-powder of diamond (Sigma Aldrich, crystals < 10 nm) diluted in water in ultrasonic bath, the second step was growth of NCD thin layer for 2, 4, or 6 h. The areas which act as working electrodes were defined to be about 2x2 mm by picein on 10x20mm area. All stock solutions were prepared from analytical grade chemicals in 18 MΩcm deionised water. A three-electrode arrangement was used in all experiments. As a reference, Ag/AgCl (0.3 mol/L KCl) electrode and, as a counter electrode, a platinum plate $10x10mm^2$ were used. Voltametric experiments were performed with an electrochemical potenciostat/galvanostat PGSTAT128N (Metrohm Autolab B.V.) with a PC.

3. Results

From previous works [3], [5] we used as optimised parameters of SW ASV the values of f= 100 Hz, sp= 5 mV, A= 0.1 V, Sr= 0.5 V, then we looked for response electrodes with different deposition parameter. The effect of NCD film growth conditions was studied in terms of gas flow ratio of CH_4 :H₂ (1-5%) (Fig. 1) and growth time (2, 4 and 6h) (Fig. 2).





Fig.2: SWV ASV NCD film growth 6:300 2h, 4h and 6h in acetate buffer, pH 4.5, Bi: 7.10^{-6} mol. l^{-1} and Me: 5.10^{-7} mol. l^{-1} .

These measurements show a maximum of striped metals for 6h growth at 2% of CH_4 in H_2 for NCD. With concentration increase of CH_4 in H_2 the electrode response was drastically decreased until no response was observed at 5%. In Raman analysis (Fig. 3) this corresponds to increase of broad band sp² C-C bonds centered at 1 580 cm⁻¹ labeled as "G" and decrease of sp³ C-C bonds centered at 1 333 cm⁻¹. Very interesting in Raman spectra is a broad band centered at 2 230 cm⁻¹ which is assigned to C-H bonding. This is clearly shown in

Fig. 4, where increase of C-H bond intensity can be clearly observed with growth time increase. This is dependence of stability of C-H bonds on surface. Hydrophobicity of H terminated surface has grown up to a contact angle with increasing deposition time from 74° and 2h to 84° and 6h.





Fig.3: Raman spectra of NCD films dep. for 2h with different CH_4 in H_2 content (1-5 %).

Fig.4: Raman spectra of NCD films dep. for 2, 4 and 6h with 6:300 CH₄ in H₂.

Construction of the electrode is very important for the stability, repeatability of measurement and economical use. For these reasons we tested the stability of electrodes. Stability test was measured in solution of analyte Bi: 1×10^{-5} mol/l and Me: 5×10^{-7} mol/l and realized for two hundred of ASV SWV cycles (pre-concentration, stabilization and striping). Each tenth cycle was calculated and a graph was created normalized to the first measured value in row (each maximum of stripped Bi(III), Zn(II), Cd(II), Pb(II)). Fig. 5 a) and b) shows maxima of stripped metals were after 30 cycles decreased from 40% to 20% disperse compared to the first value. After that value of maxima is stable around 50% to 60% for Bi, and 20-50% for metals from started value. In Fig. 5c the situation of maxima is a little bit different, after 40 cycles there was the same tendency as for 2 and 4h growth NCD, but the maximum for Bi has culminated at 80-90% and 40-80% for metals from started value. For this sample after 200 cycles the insulation layer was defected (some place was delaminated, this could change the measured current trough substrate, not trough sensitive NCD layer). From this reason we have chosen the 6h NCD growth at 6:300 CH₄ in H₂ for its ability of using the BiFE for simultaneous determination of Pb(II), Cd(II) and Zn(II) with optimized SWV parameters for 1x10⁻⁸ mol.1⁻¹ - 7.10⁻⁷ mol.1⁻¹ range of diluted metals in solutions with 100:1 bismuth-to-metals ratio.





Fig.6: SWV ASV NCD films 6h growth of 6:300 in acetate buffer, pH 4.5, Bi: 1.10^{-5} mol. Γ^1 and Me: 1.10^{-8} mol. Γ^1 - 7.10^{-7} mol. Γ^1 .

4. Results

In this paper we demonstrate the simultaneous electrochemical determination within two decades of diluted trace metals (Pb(II), Cd(II) and Zn(II)) on nano-crystaline diamond thin films with in-situ electroplating of bismuth. For electrodecreation a very cheap and easy to use insulating solution "picein" was used. The dependence of the stripping responses on the concentration of metals was linear in the range from 1×10^{-8} to 7×10^{-7} mol/l for the Cd(II) and Pb(II) and 8×10^{-8} to 7×10^{-7} mol/l for Zn(II). The stability of electrode is on very good level after 40 cycle surface stabilization to 200 cycles for 6h growth in 6:300 CH₄ in H₂.

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