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Microscopic and Voltammetric Properties of Lustrous Bismuth Deposits

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Abstract: A comparison of lustrous bismuth films, plated at glassy carbon, platinum and gold supports, is presented. The voltammetric performance of preplated bismuth film electrodes was tested using 50 µg/L In(III) and 50 µg/L Pb(II) solutions in 0.1 M acetic buffer in square wave and differential pulse modes. The influence of support material, plating solution concentration and storing conditions on the voltammetric response of BiFEs is discussed. The results of microscopic examinations revealing the deposits' morphology are also included.

Keywords: Bismuth film electrode, lead, indium, stripping voltammetry, scanning microscopy, atomic force microscopy

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Introduction

The electrochemical and analytical properties of bismuth film electrodes (BiFEs) have been extensively examined during the last ten years [1- 8]. Glassy carbon has been the most commonly applied support for bismuth films plated electrochemically.

The vast majority of bismuth films exhibited surfaces with rough topography that gave them the matt black coloration [9]. Recently, the usefulness of very smooth, silvery bismuth deposits obtained during the electrolysis of 0.17 M Bi(III) in 1 M $HClO_4$ was examined [10]. The remarkable resistance to mechanical damage that characterized these shiny bismuth films led to further investigations on their properties.

This paper presents a comparison of lustrous bismuth films, plated at glassy carbon, platinum and gold supports. The electrodes were plated from solutions with different bismuth(III) concentrations and SW or DP voltammograms of In(III) and Pb(II) were recorded. Our aim was to determine if the support material and the concentration of the plating solution (all deposits have very similar morphology) influence the voltammetric response of BiFEs.

Experimental section

Chemicals and Materials

The following reagents (analytical grade, POCH, Poland) were used without further purification: Bi_2O_3, 70% $HClO_4$, 80% CH_3COOH, CH_3COONa. The standard stock solutions containing 1 $g \cdot L^{-1}$ of Pb and In were obtained from Merck and diluted as required. A solution containing 0.17 M Bi(III) in 1.0 M $HClO_4$ was used as the stock solution for bismuth plating. It was prepared by mixing 4 g of Bi_2O_3 with 9 ml of 70% $HClO_4$, heating up the mixture to boiling until it became clear, and filtering it to a 100 mL flask which was filled up to the mark with water. The bismuth solution of the above composition is recommended for galvanic deposition of bismuth [11]. Perchloric acid was used for dissolving Bi_2O_3, because in solutions containing this acid Bi(III) ions do not precipitate after dilution, as is the case with other acids, e.g. HCl. All solutions were prepared using deionized water (Millipore Simplicity UV, Millipore Corporation, USA).

Instrumentation

Electrochemical measurements were performed using a μAutolab (GPES 4.9 software) potentiostat (Ecochemie, Netherlands) with a standard three-electrode configuration. A coil of platinum wire served as the counter electrode, and Ag/AgCl (3 M KCl) (Metrohm, Switzerland) acted as the reference one. The platinum wire was bent into an L shape and

placed in the voltammetric cell in parallel to the working electrode surface, and a distance of 0.5 cm was maintained between them. The working disc electrode (d = 2 mm, BAS, USA) was polished successively with 0.3 and 0.05 μm aqueous alumina slurries (Buehler, USA) and rinsed with water after each polishing step.

In some experiments, an additional adjustable resistor (20 kΩ or 500 kΩ, respectively) connected in series was used to increase the resistance of the electric circuit and to decrease the density of the electrolytic current. The resistor was placed between the working electrode and the potentiostat connector.

The morphology of the deposits was evaluated using a Nova NanoSEM 200 (FEI company, USA) scanning electron microscope (SEM) with a backscattered electrons' detector and with an elemental energy dispersive X-Ray microanalyser. The SEM images were used to estimate surface coverage and grain size by means of digital image processing software (Corel Photopaint 9). The microscope was used in low-vacuum mode (pressure of 60 Pa), the accelerating voltage was 18 kV, and the spot size was 4.0 – 4.5 nm. The distance of the samples from the detector was 4.9 – 5.8 mm.

Topography measurements of the samples were performed under ambient laboratory conditions with an Explorer atomic force microscope (ThermoMicroscopes, Vecco, USA). Contact mode topographic images were recorded using Si_3N_4 probes with a spring constant of 0.05 N/m and a nominal radius of curvature of 20 nm (VeccoNanoProbeTM Tips, model MLCT-EXMT-A). The images were recorded for scan areas of 5 μm x 5 μm and 50 μm x 50 μm (300 x 300 data points) and with scan rate of 3 lines/s. All images were flattened using a third-order polynomial algorithm provided with the instrument. Topography parameters, i.e. average roughness (Ra), root-mean square roughness (R rms), and average height (AvH) were calculated for at least three pictures obtained for 5 μm x 5 μm scanned areas, and expressed as means and standard deviations.

Preparation of Bismuth Films

The plating solution was deareated via Ar bubbling (10 mL solution, 10 minutes). The plating was performed in an unstirred solution until the total charge that had passed during the experiment was 10 mC (for 3 mm diameter disc) or 4.4 mC (for 2 mm diameter discs). The quality of the deposited bismuth layers was checked with an optical microscope just after plating and after a series of voltammetric experiments. After plating, the electrodes were immersed in diluted $HClO_4$ to wash off the rest of the Bi(III) solution and afterwards, finally rinsed with distilled water.

Results and Discussion

Microscopic Examination of Bismuth Films Plated on Glassy Carbon

Figure 1 shows three examples of different bismuth deposit morphologies obtained after plating on glassy carbon in 0.17 M Bi(III) in 1.0 M $HClO_4$. Bismuth films obtained after plating at -0.3 V were characterized by grain-like morphology (Figure 1b). The grains were approximately of the same size and the bismuth film's surface was smooth, which gave it a shine. Rougher surfaces tend to be less shiny. The discussed films were two-layered – the lower mirror-like layer was sprinkled with small amount of black powder. After dipping in water the silvery surface gained golden sheen. The golden sheen was probably caused by light diffused through bismuth microcrystallites.

Bismuth films plated at -1.0 V (Figure 1 c, d) were black and matt, resembling velvet. Their dendritic morphology was the cause of such appearance. Bi films plated in the presence of the additional resistor (Figure 1 e, f) were gray and matt. Their morphology was very different from that obtained after plating without the additional resistor; in the latter case the support surface was covered by tightly-packed bismuth crystals (grains or dendrites). When using the external resistor bismuth covered only 3.6 ± 0.4% of the support's surface area, despite the large charge exchanged during electrolysis (e.g. 25 mC). The glassy carbon support was dotted with isometric bismuth crystals (2.5 – 3.0 μm in size) gathered in clusters (of approximately 20 items). The distance between two clusters was approximately 25 – 50 μm. Such morphology of the film prevented the reflection of light from the surface and promoted light diffusion, which resulted in a slightly golden sheen observed after dipping them in water.

The above-described differences in bismuth film morphology determined not only the look of the exterior part of bismuth deposits, but also affected their mechanical properties to a large degree. The lustrous bismuth deposits were very adhesive and it was difficult to scratch them, whereas in the case of the other films it was possible to make a mark on their surface with a piece of dry paper. The softness of bismuth deposits plated at -1.0 V made it impossible to record good quality AFM images of their surface. These bismuth crystals were often unable to resist the pressure from the microscopic tip and during scanning the film topography was altered e.g. by rubbing out the high crystals. The AFM images of bismuth deposits taken for films deposited at -0.3V were well-defined. An example is shown in Figure 2. According to AFM results bismuth deposits were smooth (the average roughness, Ra, was equal to 35 ± 1.5 nm). The data concerning roughness, calculated for the scanned areas of the BiFE and bare glassy carbon, are shown in Table 1.

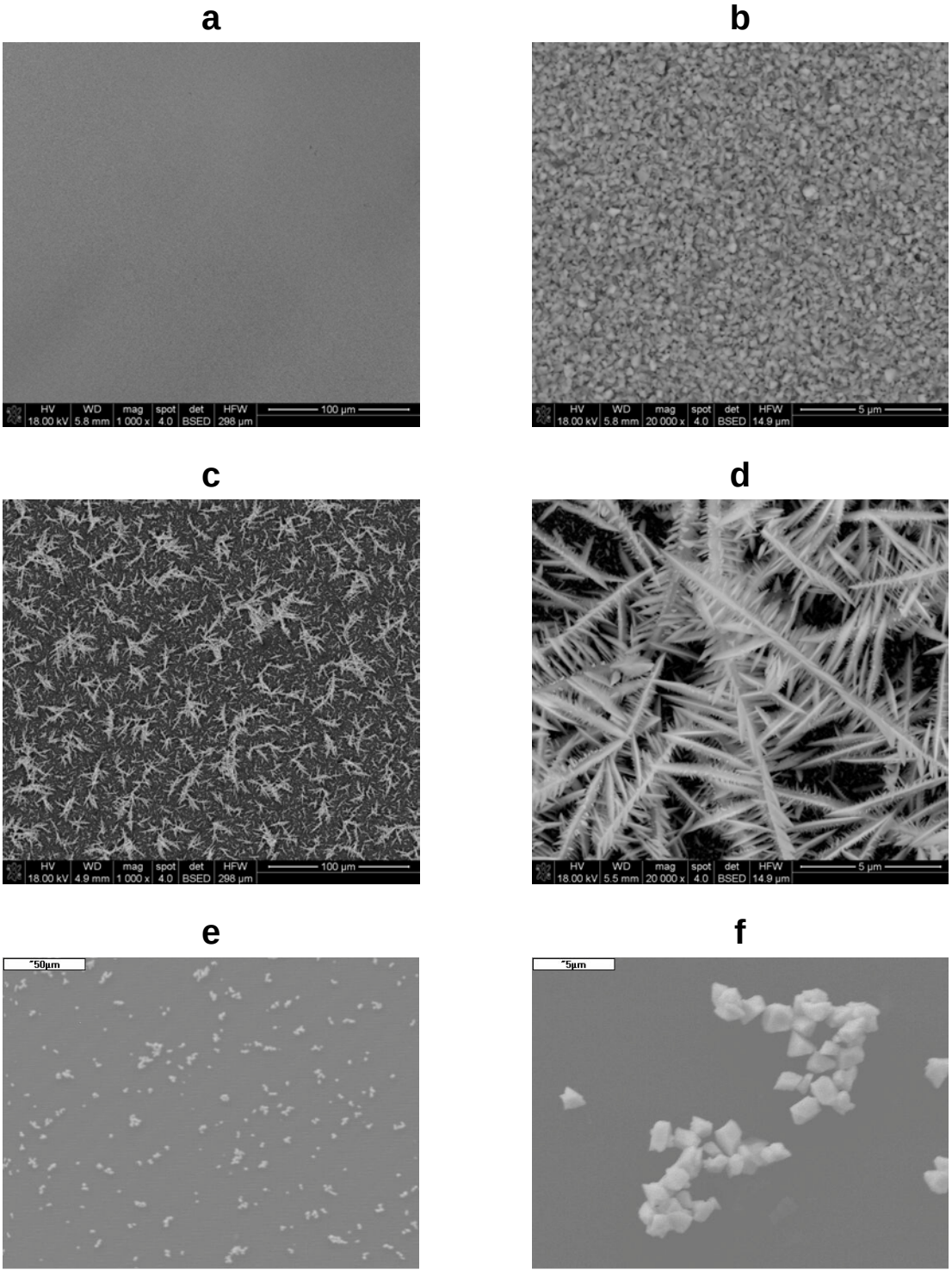

Figure 1. *SEM images of bismuth films plated on glassy carbon in a solution containing 0.17 M Bi(III) and 1.0 M $HClO_4$.* Plating potential: a) and b) E = -0.3V, c) and d) E = -1.0 V, d) and f) E = -1.0 V. In the case of d) and f) an additional 20 kΩ resistor was connected in series to the electric circuit. Plating charge: Q = 25 mC. The solution was not stirred during electrolysis.

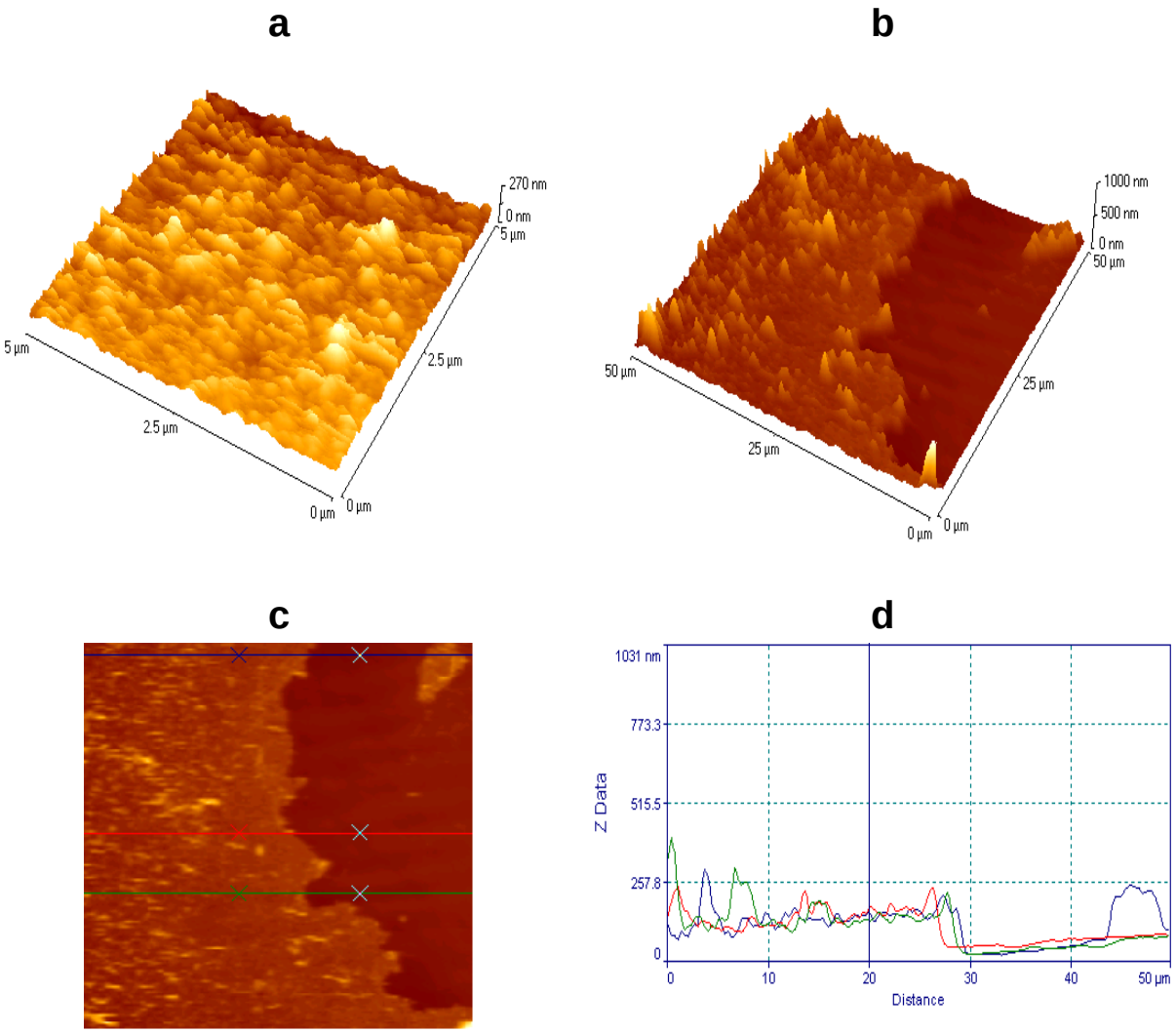

Figure 2: *AFM topographic images of glassy carbon (a) and bismuth film (b) surfaces*. An image of BiFE surface with 3 lines (c) showing bismuth film profiles (d) that were selected for the thickness calculations.

Bismuth Films Plated on Gold and Platinum

The advantageous mechanical properties of bismuth deposits plated at - 0.3 V in 0.17 M Bi(III) in 1 M $HClO_4$ encouraged us to extend the examination to other supports (Pt and Au) and other bismuth concentrations (from 0.1 mM to 100 mM). Bismuth films were deposited at three discs made from platinum, gold and glassy carbon. The seven plating solutions with different bismuth concentrations were prepared in 1 M $HClO_4$. Five plating solutions with concentrations ranging from 0.1 mM to 50 mM were stirred during plating.

Table 1: *Parameters of bismuth films deposited at -0.3 V measured using AFM.* The data are averages ± standard deviations from at least 3 scans taken at different sites of the sample

Feature	Support surface	Bismuth film surface
Ra / nm	8.3 ± 1.2	35 ± 1.5
R rms /nm	10.7 ± 2.1	53 ± 2.5
AvH / nm	65 ± 8.5	159 ± 19.5
Layer thickness / nm	-	90 – 130 (average 110)

Legend: Ra – average roughness, R rms – root-mean square roughness, AvH – average height To measure the thickness of the deposited film a scratch was made on the sample using a wooden toothpick and the image was acquired by means of AFM (Figure 2 c). The thickness of the film was measured along horizontal lines shown in Figure 2d. The calculated thickness of the bismuth deposit ranged from 90 to 130 nm.

Without stirring, it took over 600 seconds of plating to reach charge of 4.4 mC. Plating was performed without stirring in the solution with 0.1 M Bi(III). The time necessary to transport electricity in the quantity of 4.4 mC depended mainly on bismuth concentration, but it was also linked to the type of electrode material. It took longer to plate bismuth on gold and platinum than on glassy carbon. Plating on gold took, on average, 30% longer than that on glassy carbon. At the platinum electrode the bismuth coating time was, on average, 20% longer than on glassy carbon. The layers of bismuth deposited on different supports in the same plating solutions were superficially similar. The deposits obtained in solutions containing less than 0.005 M Bi(III) were grey and matt while those obtained in the more concentrated solution resembled silver in color and luster. The detailed information about the deposits obtained under different conditions is presented tabulated in Table 2. The bismuth films deposited on the gold support were very adhesive, exhibited no tendencies to peel off, and kept the same appearance for over one month when stored in air. The force of attraction between gold and bismuth film was so strong that it was difficult to remove the deposited layer even using polishing paste. It was necessary to press the electrode hard against a polishing cloth covered with powdered alumina to scratch it. In the case of platinum and glassy carbon supports it was possible to make a mark on a surface of deposited bismuth film even with a piece of dry filter paper. The bismuth film adhered more firmly to platinum than to glassy carbon. After recording several voltammetric curves the shiny bismuth deposit was

tarnished (it lost the shine to some extent) but it was homogenous and free of any visible damage. When the preplated bismuth film electrodes were stored in water for two hours they were superficially identical to those freshly prepared. These ‘soaked’ bismuth film electrodes were used in voltammetric measurements; as it turned out, their surface was not only tarnished, but also damagedto some extent. Three kinds of damage were observed: 1) the bismuth deposits became thinner – in some areas the bismuth layer was so thin that it was almost transparent; bismuth depletion started from the edge of the support disc and progressed inwards, gradually uncovering the support surface; the bismuth-free area was crescent-shaped, 2) the bismuth layer was spotted with a number of evenly distributed small holes, 3) the bismuth layer around the support edge was scattered with tiny holes. All three types of defects were observed when the gold was used as the support. The loss of bismuth film around the edge of the support in the form of holes or thinning of plated layer was observed at platinum. The films deposited at glassy carbon were not generally damaged, except for some cases where the bismuth layer around the edge of the support deteriorated after a series of voltammetric measurements.

Effect of the Concentration of Bismuth Plating Solution and the Support Material on the Voltammetric Response of In(III) and Pb(II).

The voltammetric properties of different bismuth deposits were examined using anodic stripping voltammetry (ASV) and square wave (SW) or differential pulse mode (DP). The examined solution contained 0.1 M acetic buffer and 50 µg/L of In(III) and Pb(II). The target ions were accumulated at -0.9 V for 30 or 60 seconds, and voltammetric stripping curves were then recorded from –0.9 to –0.3V . Figure 3 shows the voltammetric curves obtained at different bismuth electrodes preplated on different supports in solutions with different Bi(III) concentrations. At every examined electrode it was possible to record measureable signals originating from the oxidation process of In and Pb, accumulated at the electrode surface. The ‘quality’ of the obtained curves, determining their analytical usefulness, depended mainly on the support material. The current values measured at bismuth electrodes preplated on gold (BiFE/Au) were smallest and distorted by some random fluctuations. It was necessary to use a statistical approach (smoothing algorithms) to smooth the curves before their interpretation. The voltammetric curves obtained at BiFE/Pt were very similar to those obtained at BiFE/Au; the main difference was that the signal was less corrupted by noise.

When the 0.1 mM Bi(III) plating solution was used for BiFE/Pt preparation there was no visible evidence of bismuth film existence. The voltammograms recorded using such electrodes differ from the other curve and only one wide peak is observed (Figure 3, Pt, first curve from the top). The other curves recorded at BiFE/Pt preplated in different bismuth solutions clearly show the presence of two separate processes, i.e. indium and lead oxidation.

Table 2: *The influence of the concentration of bismuth plating solution and the support material on the visual appearance of bismuth films*

№	c_{Bi} / M	Feature	Au	Pt	GC
1	0.1	Coloration	Bright silvery deposit	Bright silvery deposit with a gold overlay	Bright silvery deposit
		Adhesion	Very adhesive, very resistant to scratch	Adhesive	Easy to scratch
2	0.05	Coloration	Bright silvery deposit	Silvery deposit with a gold overlay	Silvery deposit
		Adhesion	Very adhesive, very resistant to scratch	Adhesive	Easy to scratch
3	0.01	Coloration	Silvery with gray tarnish	Tiny, gray silver deposit	Tiny, gray silver deposit
		Adhesion	Very adhesive, very resistant to scratch	Adhesive	easy to scratch
4	0.005	Coloration	Silvery with gray tarnish	Silvery	silvery
		Adhesion	Adhesive	Adhesive	easy to scratch
5	0.001	Coloration	Gray, matt deposit	Gray, matt deposit	Gray, matt deposit
		Adhesion	Adhesive, impossible to remove using filter paper	Adhesive	easy to scratch
6	0.0005	Coloration	The support surface dusted with gray matt deposit	The support surface dusted with gray matt deposit	The support surface dusted with gray matt deposit
		Adhesion	Adhesive, impossible to remove using filter paper	Easy to remove	Easy to remove
7	0.0001	Coloration	No film observed	No film observed	Support surface covered with tiny gray powder
		Adhesion	--	--	Very easy to remove

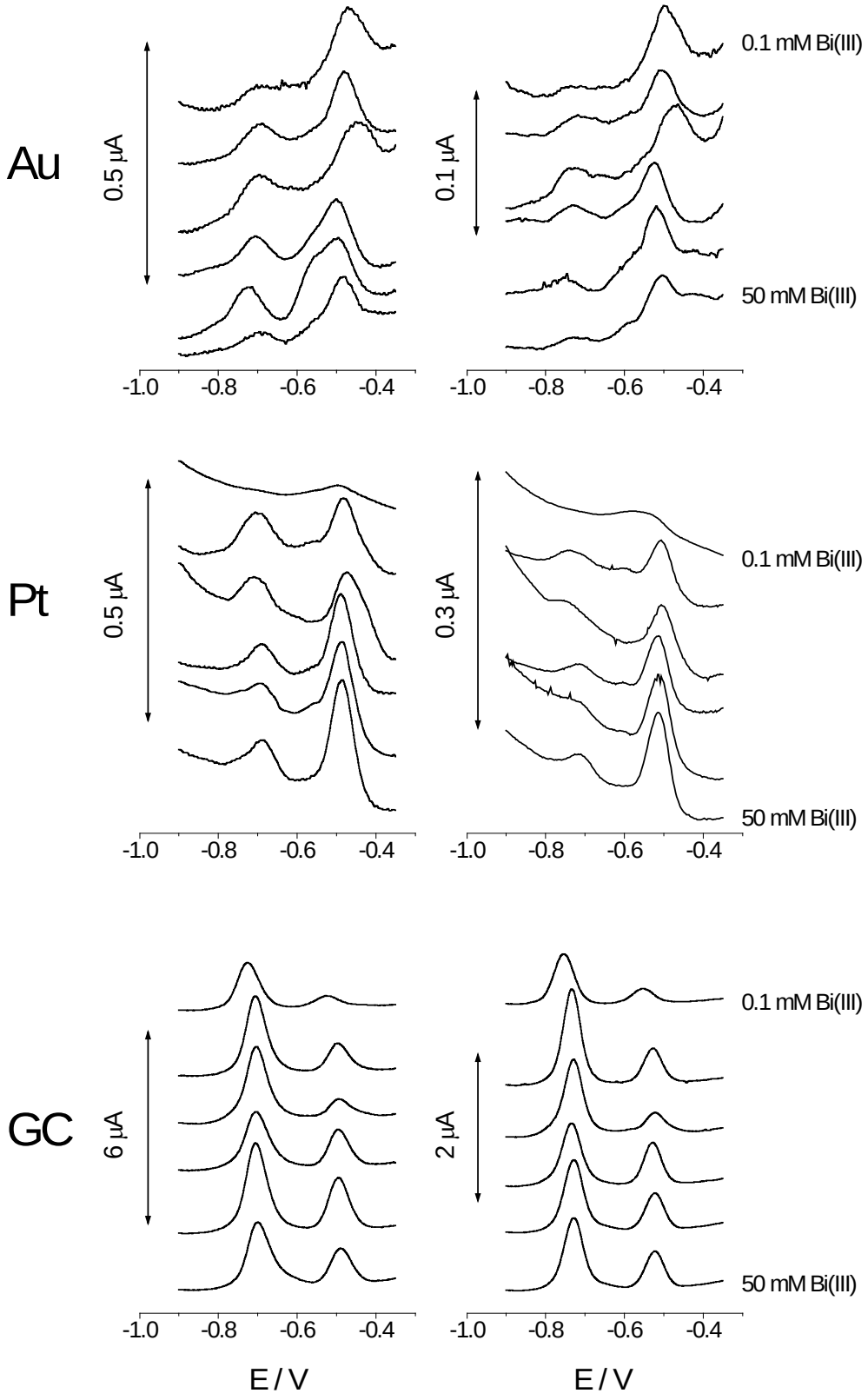

Figure 3: *The SW and DP voltammograms recorded in a solution containing 0.1 M acetic buffer and 50 µg/L of In(III) and Pb(II) at bismuth film electrodes preplated at Au, Pt and GC disks*. Plating conditions: E = -0.3 V, Q = 4.4 mC. Plating solution concentrations: 0.1 mM, 0.5 mM, 1 mM, 5 mM, 10 mM, 50 mM

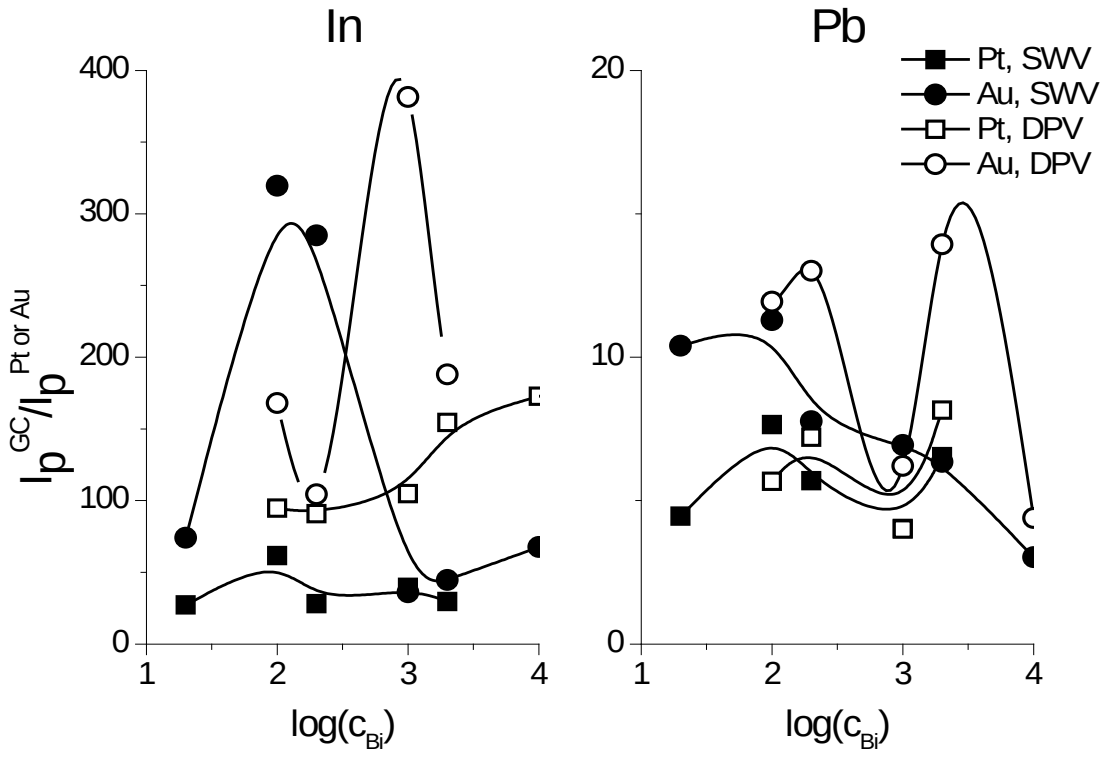

Figure 4: *The dependence of the ratio of In or Pb peak current measured at BiFE/GC to peak currents measured at BiFE/Pt* (square) *and BiFE/Au* (circle). The symbols with solid interior represent the values obtained by SWV and the open symbols represent the DPV mode. The other parameters are the same as in Figure 3.

The peaks were sufficiently distinguished from the background current to allow easy interpretation. The voltammograms recorded at BiFE/GC were conspicuously better than all curves recorded at BiFE/Au or BiFE/Pt electrodes. The SWV peaks of indium in the case of the BiFE plated in 0.01 M Bi(III) solution were as much as three hundred times higher than those recorded at other electrodes (Figure 4). The lead signals recorded at BiFE/GC were also higher but the differences in peak currents were not higher than 200-fold . In the case of BiFE/GC the peak currents of indium were always higher than those of lead. Using the BiFE/GC preplated in very diluted bismuth solution (from 0.1 mM – 1 mM) the SWV indium signals were on average 3.6 times higher than those observed for lead. Signals of indium recorded at the BiFE/GC preplated in 5 mM – 0 50 mM of bismuth were only 1.6 times higher than those for lead. The same observations were made at BiFE/GC when using the DP mode. The opposite trend was noticed when the BiFE/Pt or BiFE/Au electrodes were in use. Regardless of the polarization mode applied, the indium signals were smaller than those for lead. The difference in the value of peak potentials was about 0.2 V, and did not change significantly when the electrode support or plating solution were changed.

Conclusions

Our findings illustrate that while the application of all tested electrodes (BiFE/Pt, BiFE/Au and BiFE/GC) resulted in recording of measurable voltammetric signals of In(III) and Pb(II), the BiFE/GC offers significantly higher selectivity. At the same time the BiFE/GC is susceptible to scratching and requires taking care when using it. Bismuth films plated on gold are very adhesive which is advantageous if they are applied when the examined solution flow is forced by high pressure. The BiFEs should be used for voltammetric measurements immediately after plating. Their performance deteriorates when the preplated bismuth film electrodes are stored in water before experiments.

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