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ELECTROCHEMICAL PREPARATION OF BISMUTH NANOWIRES USING ION-ETCHED POROUS POLYCARBONATE MEMBRANE

Abstract: *Bismuth as "environmentally friendly" metal represents a promising electrode material for different electrochemical techniques. In this study, we prepared bismuth nanowires by chronoamperometry using ion-etched porous polycarbonate membrane. According to SEM-EDX analysis, obtained bismuth nanowires show uniform growth with a high aspect ratio. Due to its large surface, these nanowires have the potential to greatly improve sensor properties for the detection of a variety of inorganic and organic compounds (pollutants, drugs, etc.).*

Key words: electrodeposition, bismuth, nanowires, SEM-EDX.

INTRODUCTION

Post-transition metal bismuth has been investigated in recent years as a promising electrode material for electrochemical techniques. This is due to a negligible toxicity of bismuth and bismuth ions ("environmentally friendly" metal) and its excellent performance for electrochemical analysis tasks - comparable to well-known but toxic mercury electrodes.

Bismuth forms low-temperature alloys with heavy metals to enable preconcentrating and offers a wide negative potential window, high hydrogen overpotential, and as such, is studied for the preparation of different types of electrodes for the determination of heavy metals.[1-3]

Different types of bismuth deposits, which are used as electrodes, have been reported in the literature, such as bismuth film electrodes,[4-8] bismuth particles,[3, 9-12] bismuth bulk electrodes,[13] bismuth oxide electrodes[14]. These deposits were prepared by different methods like electrodeposition of bismuth from acidic solutions of Bi(III)-salts, by evaporation, or modification of the Bi-electrode with different molecules. Further, a large variety of substrates like glassy carbon, boron doped diamond, screen-printed electrodes, carbon nanotubes, and metal substrate have been used for bismuth electrodes.[15, 16]

Numerous studies present wide use of Bi-electrodes, for different target analytes: pharmaceuticals and drugs[17, 18]; pesticides[19, 20]; toxic organic compounds – aromatic nitro derivates[21]; biologically significant organic compounds[14, 22, 23]; food colorants[24, 25]; and most prominent for partial or simultaneous detection of toxic heavy metals.[2, 3, 6, 12, 26]

Better properties of bismuth layer shall be improved further by increasing the electrochemical active surface, that can be achieved by nanostructures namely nanowires (NWs).

In the literature, there is no data about using bismuth-nanowires (BiNWs) as sensors; what is described is only their preparation by some procedures, such as thermal evaporation[27], stress-induced method[28], alumina membrane[9, 29].

In this study, we report electrochemical preparation of BiNWs using ion-etched porous polycarbonate (PC) membrane in electroplating chamber. The advantages of this method are a low-cost set-up and easy handling with good reproducibility. The final goal is the integration of these well-characterized BiNWs onto sensor electrodes (nano sensor) for dramatically improved properties, in terms of sensitivity for analytes like heavy metals, pollutants, and drugs.

EXPERIMENTAL PROCEDURE

Electroplating chamber for BiNWs preparations

The structure of the electroplating chamber is shown in Figure 1.

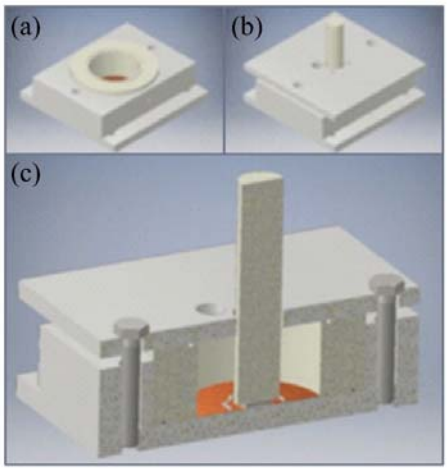

Figure 1. *Electroplating chamber for BiNWs deposition: a) base plate and centre part, b) with cover plate and c) side cross section. Picture is taken from Nick, 2015.[30]*

The chamber itself consists of a base plate, a centre part and a cover plate. The base plate serves as a base for the construction and allows the adjustment and assembling of the chamber. The middle piece contains all components required for deposition. The cover plate is needed to ensure a permanent nitrogen atmosphere.

Working electrode preparation

The working electrode (WE) was prepared by a sputtering process of metallic gold (Au) and chromium (Cr) on previously cleaned silicon wafers (Magnetron-Sputteranlage NANO 36™, Kurt J. Lesker Company). The layer thickness was 100 nm for Au and 10 nm for Cr.[31] The preparation of Au-Cr-Si wafers (further in the text "wafer") is graphically presented in Figure 2a.

Electrolyte preparation

All chemicals (bismuth nitrate pentahydrate $Bi(NO_3)_3{\times}5H_2O$; nitric acid HNO_3; dichloromethane CH_2Cl_2 and acetone $(CH_3)_2CO$) were purchased by Carl Roth (Germany) and were p.a. grade. All solutions were prepared using deionized water. The electrodeposition bismuth solution was prepared dissolving exact mass of $Bi(NO_3)_3{\times}5H_2O$ in nitric acid solution defined concentration.

Preparation of bismuth deposits

Electrochemical experiments were carried out using a potentiostat (VersaSTAT 4, Princeton Applied Research, Ametek). Deposition of bismuth was obtained using a chronoamperometry in three electrode system, with a gold electrode as working electrode (WE), a gold mesh as counter electrode (CE) and Ag/AgCl as reference electrode (RE) in the electroplating chamber. The non-polarizable reference electrode allows for a very precise adjustment of the applied voltage.

Before deposition, wafers were cleaned with deionized water and acetone to remove impurities from surface, and dried with nitrogen gas. Wafers were kept on 25 °C during the deposition process with a digital hotplate (Stuart, Germany). The squared deposition area (c.a. 0.25 cm^2) on the wafer was defined using Kapton tape. The gold WE is suitable for examining the reduction of Bi^{3+} in acidic nitrate solutions.[32]

Bismuth layer deposition

A thin Bi layer was deposited on the Au-Cr multilayer by chronoamperometry under the potential of -0.25 V for 360 s using a solution of nitric acid (0.5 M) with 0.02 M Bi^{3+} (Figure 2b).

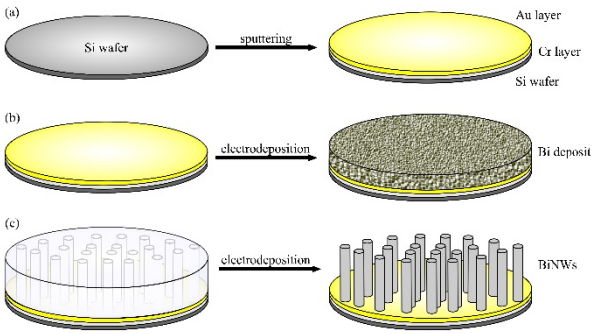

Figure 2. Shematic presentation of *fabrication process of: a) working electrodes, b) bismuth planar deposit and c) BiNWs deposit.*

Bismuth nanowire deposition

BiNWs were obtained, using ion-etched porous polycarbonate (PC) membrane with a pore diameter of 200 nm and a density of $6{\times}10^8$ pores/cm^2 (Whatman, United Kingdom). The electrochemical process was performed in a solution of 0.1 M Bi^{3+} in nitric acid (0.1 M) at a potential of -0.5 V for 3600 s. A controlled nitrogen atmosphere allowed to exclude ambient air and thus reduce the oxygen content in the deposited material. After deposition, the PC membrane was dissolved in dichloromethane, while the Kapton tape was treated with acetone and then carefully removed with tweezers, Figure 2c. The procedure of preparing BiNW is similar like the procedure presented for gold wires by Nick in 2015.[30]

Characterization of deposits

Information of bismuth deposits were obtained by Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) (Phenom-World, Netherlands).

RESULTS AND DISCUSSION

The current curve during the chronoamperometric deposition of the bismuth layer and BiNWs deposition is shown in Figure 3. The current (negative values) grows fast in the beginning and then stabilizes at a constant value which represents the formation of bismuth growth and the growth of bismuth layer (Fig. 3a). The current curve in Figure 3b shows the formation of BiNWs. In the first few seconds, the deposition process takes place within the cavity that is formed by the membrane and the wafer (increase in the current values). Afterwards, wires grow evenly in the nanopores of the membrane, and due to this a nearly constant current is established.

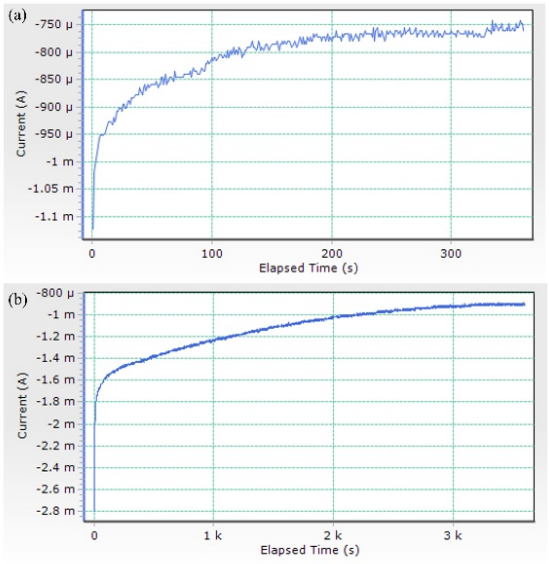

Figure 3. *Current change during bismuth deposition (a) layer without PC membrane (b) BiNWs with PC membrane.*

In this experimentm, we did not allow for overgrowth of the wires, but the beginning of overgrowth can be noticed by a sudden increase of the curent magnitude, and begin when wires grow above the membrane and then form a layer.[30, 31] The gold WE shows a reduction current starting at -0.65 V, which is about 10 mV negative of the reversible hydrogen potential.[32]

Scanning electron micrographs of bismuth deposits are shown on Figure 4.

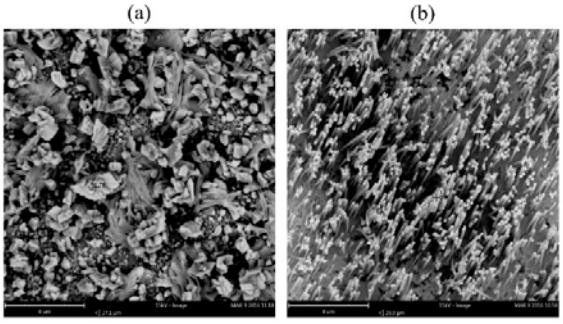

Figure 4. *SEM micrographs of surfaces of (a) bismuth thin layer and (b) BiNWs.*

Figure 4a shows nonuniform formation of bismuth layer on gold with deposits of different sizes. Using the ion-etched porous PC membrane a uniform and parallel wire growth is possible which determines the density and geometry of the wires (Figure 4b), similar like in Jin et al. (2003)[29]. An important advantage of the usage of PC membranes for BiNWs preparation is that it can easily and fast be removed with dichloromethane, achieving freestanding nanowires with extremely high aspect ratio of 100 and active surface.

EDX spectra of obtained BINWs are shown in Figure 6. Under investigated conditions, we achieved thin layers and nanowires with a high percent of bismuth, 100% for deposition without membrane (Fig. 6a) and 96% for deposition with membrane. A small percent of carbon (approx. 4%) which peak are noticed in EDX spectrum (Fig. 6b) is probably a rest of the PC membrane which was not completely dissolved with dichloromethane.

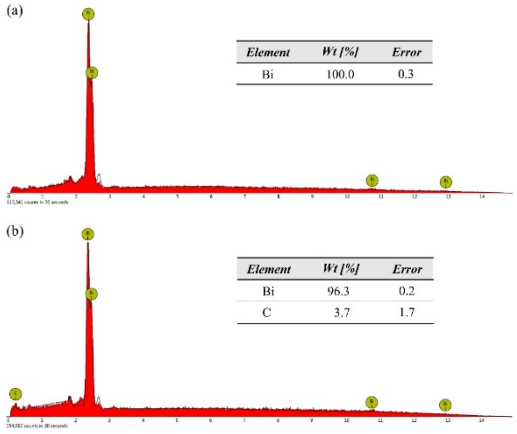

Figure 6. *EDX spectra of (a) bismuth layer and (b) BiNWs*

Also, these spectra show that we were able to deposit bismuth without any additional elements (except C in small %), which is important to achieve high quality sensor functionality.

Prepared nanowires have the potential to improve nano-sensors for the determination of organic and inorganic compounds (pollutants, drugs, etc.). The integration will be subject of our further investigations.

CONCLUSION

In this study, we achieved uniform bismuth-nanowires growth using ion-etched porous polycarbonate membranes for an easy and low-cost electrochemical deposition process. Membranes can easily be removed after electrodeposition process, which contributes to the creation of free space between the wires and a high active surface of the wires. The gold layer in the multilayer system is suitable as a working electrode for monitoring the reduction of bismuth (III) in the acidic nitrate solution.

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BIOGRAPHY

Nenad S. Krstić was born in Vranje, Serbia, in 1984.
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ELEKTOHEMIJSKO DOBIJANJE BISMUT NANO-ŽICA KORIŠĆENJEM POROZNE POLIKARBONATNE MEMBRANE

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Rezime: *Bizmut kao ekološki prihvatljiv metal, predstavlja obećavajući elektrodni materijal za različite elektrohemijske tehnike. U ovoj studiji hronoamperometrijski smo pripremali bizmut nano-žice korišćenjem porozne polikarbonatne membrane. Prema SEM-EDX analizi, dobijene bizmut nanožice pokazuju uniformni rast sa visokim odnosom dužina žice - prečnik. Zahvaljujući svojoj velikoj površini, ove nano-žice imaju potencijal da značajno poboljšaju osobine senzora za detekciju raznih neorganskih i organskih jedinjenja (zagađivači, lekovi, itd.).*

Ključne reči: elektrodepozicija, bizmut, nano-žice, SEM-EDX.