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ScienceDirect

Electrochemistry Communications 9 (2007) 2507–2513

electrochemistry communications

www.elsevier.com/locate/elecom

Formation of the bismuth thiolate compound layer on bismuth surface

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Received 3 July 2007; received in revised form 18 July 2007; accepted 20 July 2007
Available online 31 July 2007

Abstract

The structure and composition of thiolate multilayers formed at bismuth monocrystal electrodes from solutions of 1-octadecanethiol and 1-decanethiol in ethanol at open circuit potential are characterized by cyclic voltammetry, electrochemical impedance and infrared reflectance spectroscopy, optical microscopy and AFM methods. Analysis of results demonstrates that after holding of Bi(hkl) electrodes during some hours in solution of thiol in ethanol bismuth is covered with a thick porous layer of bismuth thiolate compound. For the verification of formed thiolate layers the new compounds tris(1-octadecylthio)bismuthine and tris(1-decylthio)bismuthine were also synthesised from bismuth(III)oxide and thiol in hexane solution and a similarity of properties with the bismuth thiolate compounds, formed at the bismuth electrode surface, has been demonstrated.

Keywords: Bismuth; Single crystal; Bismuthine; Multilayer; Thiol; Thiolate

1. Introduction

Self-assembled thiol monolayers on gold have been studied extensively and various interesting nanotechnological applications have been demonstrated [1–4]. Thiols also interact with other metal surfaces and thiol monolayers have been detected on Ag, Cu, Pt and other metal electrodes [2,4,5]. Even if the metal electrode is coated with thin surface oxide layer a monolayer of thiol is still self-assembled as it was found using X-ray photoelectron spectroscopy method [6]. Some works even propose the formation of thiol multilayers at certain conditions on Cu, Ag and Hg electrodes [7–9]. Bismuth seems to interact strongly with thiols because a thiol cotton fiber adsorbs more strongly Bi(III) ions than Ag(I), Cd(II) or other heavy metal cations [10]. However in electrochemical literature there is only one study reporting the formation of self-assembled hexadecanethiol and other thiol monolayers on bismuth surface [11]. In this article there is no data about the thickness of the thiol layer formed at bismuth electrode and this layer was characterised only by its diffusion blocking properties of electroreduction reaction of daunomycin and picric acid at bismuth electrode surface.

In this work bismuth monocrystal electrodes were modified with 1-octadecanethiol (ODT) or 1-decanethiol (DT) in ethanol solution at open circuit potential (OCP) and the properties of the surface layers formed have been characterised by various methods. In addition the synthesis method of these bismuth thiolates has been worked out.

2. Experimental details

2.1. Preparation of bismuth electrode

Bismuth monocrystal bars were cleaved through Bi(1 1 1) and Bi(0 0 1) interfaces at the temperature of liquid nitrogen. Then these pieces were processed to 4.00 mm cylinders and glued into 4.05 mm (inner diameter) borosilicate glass tube (Duran glass from Schott) using two component transparent epoxy glue. The final surface preparation of a Bi(hkl) electrode was obtained by electrochemical polishing in KI + HCl solution under positive potential at ~200 mA for 4 s at rotation speed 180 rpm [12,13].

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doi:10.1016/j.elecom.2007.07.029

2.2. Procedure for thiolate coating

After polishing the electrode surface was thoroughly rinsed with ultra purified water and ethanol. Surface modification with thiol has been made by keeping the Bi monocrystal electrode in the 1 mM thiol (1-octadecanethiol or 1-decanethiol) solution in 96% ethanol for 24 h at OCP. Before measurements the electrode was washed thoroughly with 10 mL of ethanol and with ultra pure water (MilliQ+).

2.3. Apparatus and reagents

The electrochemical measurements were carried out using Autolab PGSTAT 30 with a FRA 2 system in a typical three-electrode cell using Ag|AgCl reference electrode in saturated KCl solution (all potentials mentioned in the following chapters are measured against this reference electrode). Solutions for electrochemical measurements have been made from $LiClO_4$ (Sigma Aldrich 99.99%) and were saturated with electrolytic hydrogen (Barken BALSTON hydrogen generator, purity >99.9999%) during 30 min prior measurements to remove dissolved oxygen.

FTIR spectroscopy measurements were made using Perkin Elmer Spectrum GX system, equipped with VeeMaxII mirror system from Pike Technologies. Nitrogen-cooled mid-range MCT detector was used for grazing angle measurements using *p*-polarized light incident at 80° angle. The resolution was 4 cm^{-1} and the spectra were collected during 2 min (256 coadded scans) in 99.996% argon atmosphere. The reference spectrum was obtained using the same electrode before modification it in concentrated thiol solution in 80% ethanol for 60 s. This quicker method for thiol coating of bismuth was used to keep the time between reference and sample measurements as short as possible with the aim to eliminate the detector drift with time.

For synthesis of the bismuth thiolate compound the following substances were used: *n*-hexane (Fluka $\geqslant$ 99.0%), Bi_2O_3 (pure for analysis, additionally heated at 500 °C for 5 h), 1-octadecanethiol (Sigma Aldrich > 98%) and 1-decanethiol (Sigma Aldrich > 96%).

Meiji MX 8530 reflective light optical microscope was used for inspecting the thiol modified bismuth surface. AFM pictures were taken with Molecular Imaging PicoSPM microcope with PicoAFM scanner using Veeco NanoProbe™ probing silicon nitride tips.

3. Results and discussion

3.1. AFM and optical microscopy images

Fig. 1a shows an AFM image of electrochemically polished Bi(0 0 1)^{EP} surface. There might be some oxide layer contribution to the surface roughness as the picture was taken in air environment, although the surface of Bi(0 0 1)^{EP} is never as smooth as the cleaved Bi(1 1 1) mono-

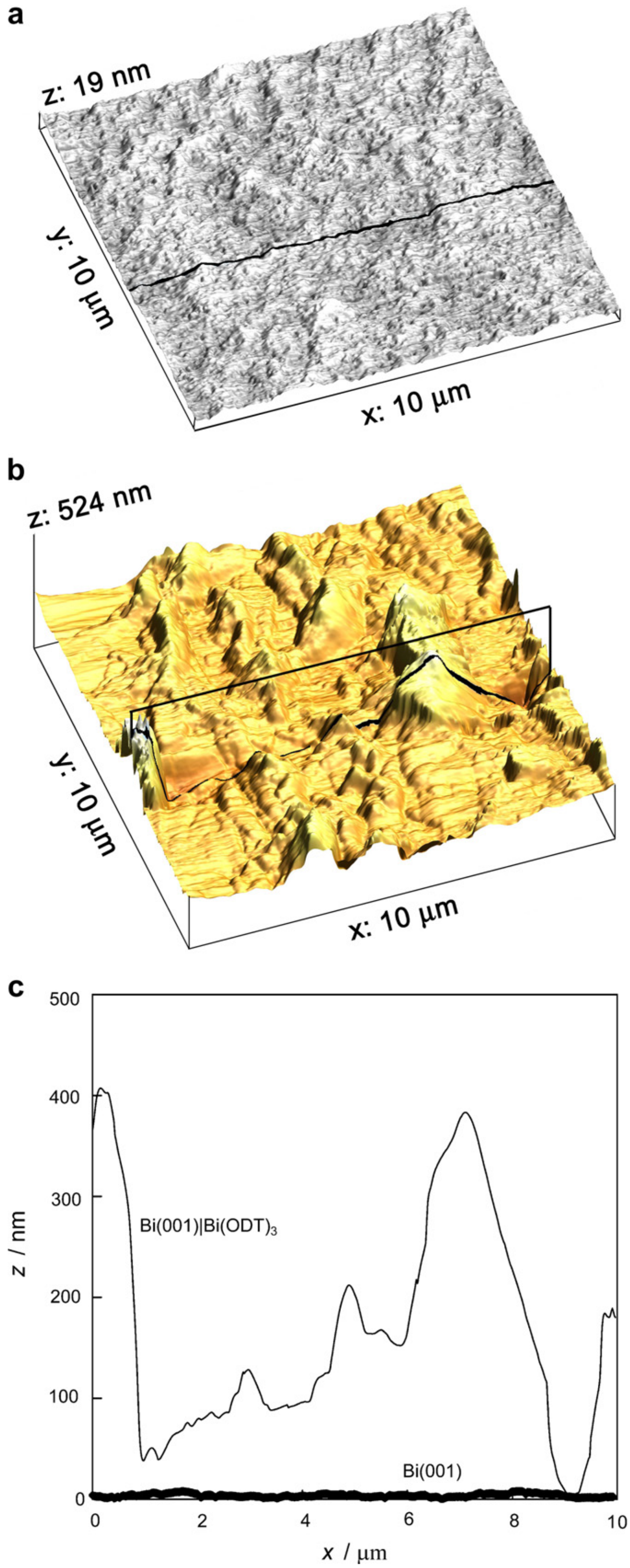

Fig. 1. 10 × 10 µm AFM images for electrochemically polished Bi(0 0 1) electrode surface (a) and after modification with 1-octadecanethiol (ODT) solution in ethanol at open circuit potential (OCP) (b). (c) Height profiles for these interfaces, noted in figure.