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EQCM study on the oxidation/reduction of bismuth sulfide thin films

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ABSTRACT

The oxidation/reduction of bismuth sulfide thin films deposited on an Au electrode using the successive ionic layer adsorption and reaction method has been investigated by electrochemical quartz crystal microbalance combined with cyclic voltammetry and X-ray photoelectron spectroscopy. It has been shown that the oxidation/reduction of bismuth sulfide film depends on the nature of anion. In the acetate solution the bismuth sulfide film is oxidized at more negative potential values than that in sulfuric acid solution. During the oxidation of bismuth sulfide film the Bi present on the surface of the bismuth sulfide film is oxidized first. This process is followed by subsequent oxidation of bismuth sulfide film alongside the oxidation of Au. In the acetate background solution the oxidation of bismuth sulfide occurs with the whole film stripping and the calculated amount is related to the amount of deposit and corresponds to the thickness of $\sim$9–10 nm. In sulfuric acid the bismuth sulfide film is not completely stripped out in one anodic cycle. The evaluated amount during the first anodic scan corresponded to the thickness of deposit of $\sim$3–4 nm. The reduction of bismuth sulfide film took places at more positive potential values in the acetate background solution than that in sulfate background solution at pH 4. After the reduction of bismuth sulfide film to Bi^0 and S^{2-} in the background solution, depending on the nature of anion, the oxidation of metallic Bi proceeds by two different mechanisms: in the sulfate solution Bi is oxidized to Bi(III) oxygen compounds while in the acetate solution Bi is oxidized by dissolution.

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1. Introduction

Thin films of bismuth sulfide show promise for application as photovoltaic converters, optoelectronic and thermoelectric devices, and photodiode arrays. Currently they have been used as a conductive sublayer in direct electrochemical metallization of dielectrics. For this purpose bismuth sulfide is usually formed using the successive ionic layer adsorption and reaction (SILAR) method which is simple, low-cost and convenient for large area deposition. A necessary step to induce metal electrodeposition is the reduction of metal sulfide to metal. Investigation of electrochemical behavior of thin bismuth sulfide film deposited on an electrically conductive electrode by the SILAR method in the supporting electrolytes (metal-free) is important both from the fundamental and practical points of view and requires detailed studies.

Electrochemical quartz crystal microbalance (EQCM) is a very sensitive technique which allows a precise study of electrochemical reactions by simultaneous measuring the current, charge and related mass changes on the working electrode. This technique has been widely used for investigation of electrochemical deposition of binary [1–9] or ternary chalkogenides [10–12]. In our

previous publications [13–16] we studied the electroreduction of bismuth sulfide layers deposited on gold and glassy carbon (GC) electrodes in both the metal plating solutions as well as in the supporting ones. It was shown that the bismuth sulfide can be easily modified in nickel and zinc plating electrolytes. The bismuth sulfide initiates the reduction of Ni^{2+} and Zn^{2+} before their overpotential deposition (OPD). Thus, after modification of bismuth sulfide film with Ni and its annealing at temperatures higher than 120 °C a metal-rich mixed sulfide $Ni_3Bi_2S_2$ (parkerite) was obtained, which possesses a markedly higher conductivity [13].

The present work is a continuation of our previous studies. The influence of the anion nature on the oxidation/reduction of bismuth sulfide film in the supporting solutions was studied in more detail by means of EQCM combined with cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS). The possibility to evaluate the amount of bismuth sulfide film deposited by the SILAR method was examined.

2. Experimental

Bismuth sulfide films were deposited on the quartz crystal sputtered with Au for CV and EQCM measurements using the SILAR method. For the formation of bismuth sulfide layers the working microbalance electrode was mounted in-between two silicone

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rubber o-rings which were placed between the holder and a glass tube forming the bottom of the cell of a working volume of *ca.* 2 ml. The modification of Au with bismuth sulfide was performed according to the following procedure: (a) adsorption of Bi(III) by dropping 2 ml of a solution containing 0.08 M $Bi(NO_3)_3$ and 1.2 M aminoacetic acid (pH 6, which was adjusted with a solution prepared from $Na_2B_4O_7\cdot10\ H_2O$) for 2 min; (b) rinsing of the treated surface with deionized water; (c) sulfidation by dropping of 2 ml of a solution containing 0.064 M Na_2S and 0.4 M NaOH for 1 min; (d) rinsing of the treated surface with deionized water. Finally, the electrode was taken out of the holder and dried in air. This constitutes one deposition cycle (N) of the bismuth sulfide film. The whole cycle described was carried out repeatedly for the required number of deposition cycles. The simultaneous CV and microgravimetry scans were carried out on a previously deposited two layers of bismuth sulfide on an Au electrode (N = 2).

The EQCM system employed was the same as that in [17,18]. Simultaneous cyclic voltammetry and the microgravimetric studies were performed with a precision frequency counter Č3-64, a home-built 6 MHz frequency oscillator, two digital voltmeters B7-46/1 connected to a PC through the IEEE 488 interface, a programming potentiostat PI-50-1 and a sweep generator PR-8 (Russia). AT-cut quartz crystals of 6 MHz fundamental frequency (from Intellemetrics Ltd., UK) sputtered with gold from both sides were used. A standard three electrode configuration was employed with one side of the quartz crystal as a working electrode, an Ag/AgCl/KClsat electrode as reference, and a Pt-wire as a counter electrode. The geometric area of the working electrode was 0.636 cm². The measured electrode potential, the current and the frequency (the stability ± 0.5 Hz) were transferred to the PC every 1.3 s. In the text, the electrode potentials are given with respect to the reversible hydrogen electrode (RHE) or the standard hydrogen electrode (SHE). The cyclic voltammograms and microgravimetric scans were recorded at a sweep rate of 5 and 10 mV s⁻¹.

For the experiments of the reduction of bismuth sulfide two types of background solutions at pH 4 were used:

(a) Sulfate (M): Na_2SO_4 – 0.05, H_3BO_3 – 0.32.
(b) Acetate (M): $Na(CH_3COO)$ – 0.05, H_3BO_3 – 0.32.

For the experiments of the anodic oxidation of bismuth sulfide 0.5 M sulfuric acid and background acetate solutions were used.

Combined gravimetric and coulometric data allow calculating the number of the electrons involved in the reaction. EQCM measurements are based on Sauerbrey's equation [19] where the measured frequency changes of the quartz crystal are correlated with the mass changes:

$$\Delta f = -2\frac{f_0^2 \Delta m}{S\sqrt{\mu_q \rho_q}} = -K\Delta m \tag{1}$$

where f_0 is the resonant frequency of the quartz crystal, S is the piezoelectrically active area (cm²), μ_q is the shear modulus of the quartz (2.947×10^{11} g cm⁻¹ s⁻²) and ρ_q its density (2.648 g cm⁻³) [20]. K includes all the constants of Eq. (1) and for fundamental resonance frequency of 6 MHz is equal to 128.152×10^6 Hz g⁻¹ corresponding to a sensitivity of 12.26 ng Hz⁻¹ cm⁻².

According to Faraday's law, the charge passed during the electrochemical reaction can be expressed as

$$Q = \frac{Fz\Delta m}{M} \tag{2}$$

where F is the Faraday constant (96,500 C mol⁻¹), z is the number of electrons involved in the reaction, Δm is the mass change during the reaction, and M is the molar mass of the corresponding chemical species. By combining Eqs. (1) and (2), it is possible to determine the ratio m/z by plotting the measured frequency change (Δf) as a function of the charge consumed (Q):

$$\frac{m}{z} = \left|\frac{d\Delta f}{d\Delta Q}\right|\frac{F}{K} \tag{3}$$

The detail derivative of this equation is described in [6,7].

Elemental analysis of deposits was studied by XPS. The XPS analysis was performed by using an "ESCALAB MK II" spectrometer (VG Scientific, UK) equipped with a Mg Kα X-ray radiation source (1253.6 eV) operated at 300 W, at a fixed pass energy of 20 eV. The pressure of 1.33×10^{-6} Pa was kept in the UHV analysis chamber. To obtain depth profiles, the samples were etched in the preparation chamber with ionized argon under vacuum of 5×10^{-4} Pa. The accelerating voltage of ca. 1 kV and the beam current of ~20 μA cm⁻² were used which corresponded to the etching rate of ~4 nm min⁻¹. The XPS spectra were recorded for Bi4f7/2, S2s and O1s. The sensitivity factors of these elements were taken from [21]. The spectra obtained were compared with the standard ones [22–24].

All chemicals were of analytical grade.

3. Results and discussion

3.1. Characterization of bismuth sulfide film

Two layers of bismuth sulfide thin film were deposited on the Au electrode using the SILAR method. The purity and composition of the as-deposited bismuth sulfide sample was characterized by XPS analysis. The data of XPS analysis are given in Table 1 and Fig. 1. No elements other than Bi, S, O and Au were detected, indicating the high purity of the resulting product. The XPS sputter spectrum in depth for Bi 4f7/2 is illustrated in Fig. 1a. The two strong peaks in Fig. 1a at 156.7 and 157.9 eV corresponded to the Bi 4f7/2 transitions [21,24], and the peak at 225.2 eV (Fig. 1b) can be attributed to the S2s binding energy [21,24]. The surface coverage θ of bismuth sulfide was calculated by an analysis of the XP spectra according to the equation [25]:

$$\theta = \frac{A_{Bi}/S_{Bi} + A_S/S_S}{\sum_i A_i/S_i} \quad \text{where } i = Bi, S, O, Au \tag{4}$$

The ratio A_i/S_i is proportional to the surface concentration of the element i, and A_i and S_i represent the corresponding XPS peak areas and sensitivity factors, respectively. The θ value of 78% was estimated from the experimental spectra in Fig. 1 for a modified gold surface.

The thickness of bismuth sulfide films deposited on glass sheets using the same solutions as those in this study was determined gravimetrically [26]. The authors showed that the thickness of one-cycle bismuth sulfide layer is approximately 0.9 ± 5 nm. After two deposition cycles the thickness of bismuth sulfide layer is 4.4 ± 1.1 nm. When the number of deposition cycles is five, the thickness of deposit is 21.8 ± 2.3 nm. The average growth rate was 5 nm per cycle on the glass sheets.

The elemental composition of bismuth sulfide film deposited on glassy carbon using the same solutions as those in this study was also examined in previous studies by energy dispersive analysis of X-rays (EDAX) [13] and X-ray diffraction (XRD) [14]. It was determined that the varying film thickness from 4 to 15 deposition cycles, the stoichiometric ratio Bi/S does not depend on the film thickness and is very close to the theoretical one −0.66 [13]. Inasmuch as the deposited bismuth sulfide film is amorphous, it was transferred into the crystalline state by heating at 150 °C under vacuum for 6 h. The XRD patterns of bismuth sulfide film shows diffraction peaks attributed to Bi_2S_3 (PDF 17-320) and metallic Bi (PDF 44-1246) [14]. According to the results obtained, it may be