EQCM Study of Influence of Anion Nature on Electrochemical Reduction of Bismuth Sulfide in Nickel Plating Solution

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The influence of anion nature on the reduction of bismuth sulfide film deposited on gold using the successive ionic layer adsorption and reaction method in solutions containing Ni^{2+} ions has been investigated by electrochemical quartz crystal microbalance combined with cyclic voltammetry and X-ray photoelectron spectroscopy. It has been determined that the reduction of bismuth sulfide film in the nickel plating solution depends on the anion nature: larger cathodic current and mass changes (Δf) are observed in the solution containing acetate anion as compared to those in the solution containing sulfate anion. As the reduction of bismuth sulfide film in the background solutions depends on the nature of anion, it influences the cathodic reduction of Ni^{2+} ions prior to OPD of Ni. A greater current and mass change (Δf) is conditioned by simultaneously occurring reduction of bismuth sulfide film when the film is reduced in the acetate nickel plating electrolyte in contrast to that in the sulfate one.

Keywords: bismuth sulfide, nickel, SILAR, EQCM, XPS.

INTRODUCTION

Thin films of metal sulfides show promise for application as photovoltaic converters, optoelectronic and thermoelectric devices, and photodiode arrays. Recently they are used as a conductive sublayer in direct electrochemical metallization of dielectrics. For this purpose metal sulfide films are easily formed on dielectrics surfaces using the successive ionic layer adsorption and reaction (SILAR) method. This method is simple, low-cost and convenient for large area deposition. Successful direct metallization onto modified dielectrics surfaces or electrically conductive substrates has been proposed using the films of non-stoichiometric copper sulfide [1–6], zinc sulfide [7], cobalt sulfides [8–17], nickel sulfide [18]. Bismuth sulfide films have also been proposed for direct metallization of dielectrics [19]. The present study is continuation of our previous papers discussing reduction of bismuth sulfide thin films in nickel plating electrolytes as well as in supporting ones [20–22]. The detailed studies were carried out to investigate the reaction mechanism of electroreduction of bismuth sulfide film in both the nickel plating electrolyte and supporting ones by means of electrochemical quartz crystal microgravimetry (EQCM) [21, 22]. It has been shown that the bismuth sulfide initiates the Ni deposition prior to overpotential deposition (OPD) of it. The processes occurring during the reduction of bismuth sulfide film in the Ni^{2+}-containing electrolyte depend on the electroreduction medium [22]. As the reduction of bismuth sulfide film in the supporting electrolytes was determined to depend on the nature of anion [23], in the present study we investigated the influence of anion nature on the reduction of bismuth

sulfide film in the nickel plating solution in more detail by means of EQCM combined with cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Prior to measurements, the bismuth sulfide films were deposited on Au using the SILAR method. The details of the experimental method were described previously in [22–24]. Briefly, 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 $Na_2B_4O_7 \cdot 10\,H_2O$) 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. This constitutes one deposition cycle (N) of the bismuth sulfide film. In the present study the bismuth sulfide layers were formed on the gold electrode by two deposition cycles ($N = 2$) at room temperature.

The details of the quartz crystal microbalance (EQCM) set-up employed are described elsewhere [25, 26]. 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 frequency (from Intellemetrics Ltd., UK) sputtered by gold from both sides was used. A standard three-electrode configuration was employed with one side of the quartz crystal, as a working electrode, an $Ag/AgCl/KCl_{sat}$ electrode as reference, and a Pt-wire as a counter electrode. The geometric area of the working

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electrode was 0.636 cm^2. The measured electrode potential, the current and the frequency (the stability ±0.5 Hz) were transferred to the PC every 1.3 s. The electrode potentials are given with respect to the standard hydrogen electrode (SHE). The cyclic voltammograms and microgravimetric scans were recorded at a sweep rate of 5 mV s^{-1}. All experiments were carried out at 20 °C.

The experiments were carried out using the Ni plating solutions: 0.05 M NiSO$_4$, 0.32 M H$_3$BO$_3$ and 0.05 M Ni(CH$_3$COO)$_2$, 0.32 M H$_3$BO$_3$. The solution pH was 4. Analytical grade chemicals were used to prepare solutions.

EQCM measurements are based on Sauerbrey's equation [27] 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 (cm^2), 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}) [28]. K includes all the constants of equation (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}. This corresponds to the sensitivity of the QCM used 0.081 Hz ng^{-1} cm^2.

Elemental analysis of the deposits was studied by XPS. The XPS analysis was performed by using an "ESCALAB MK II" spectrometer (VG Scientific, UK) equipped with an Mg K$_\alpha$ X-ray radiation source (1253.6 eV) operated at 300 W, at 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 Bi4f$_{7/2}$, S2s, O1s and Ni2p$_{3/2}$. The sensitivity factors of these elements were taken from [29]. The spectra obtained were compared with the standard ones [30–32].

## RESULTS AND DISCUSSION

The dependence of the anions nature on the reduction of bismuth sulfide film in solutions containing Ni^{2+} ions has been investigated. Figure 1 represents the cyclic voltammograms for the current (Fig. 1, a) and frequency changes (Fig. 1, b) measured in a Ni plating solution containing sulfate (solid line) and acetate (dashed line) anions at pH 4. The electrode potential was swept in the cathodic direction up to –0.4 V until the bulk Ni starts. In our previous studies [13–15] it was shown that the bismuth sulfide film initiates the reduction of Ni^{2+} before the overpotential deposition (OPD) of Ni. As seen in Fig. 1, in the recorded CV one cathodic peak C at a potential of –0.3 V is observed with the electrode mass increase. This cathodic peak C reflects the Ni^{2+} reduction before OPD of Ni.

In our previous publication [23] it has been shown that the reduction of bismuth sulfide film in the background solution free from metal ions depends on the nature of

anion: the reduction of bismuth sulfide film took place at more positive potential values in the acetate background solution than that in the sulfate background solution at pH 4. The reduction peak of bismuth sulfide film in the acetate background solution is at –0.4 V (Fig. 2, b, cathodic peak C1) and that in sulfate solution at –0.55 V (Fig. 2, a, cathodic peak C1). The cathodic currents in both cases are followed by mass increase indicating that the bismuth sulfide film is reduced to Bi^0 and S^{2-} as was confirmed in ref. [23]. According to the XPS data in ref. [23], the bismuth sulfide film is reduced completely in the acetate background solution in contrast to the sulfate one. When comparing the data obtained during the reduction of bismuth sulfide film in the background electrolytes (compare Figs. 1 and 2 [23]) and those in the nickel plating electrolyte at pH 4, it is seen that in the case of acetate anion, the potential regions of cathodic peaks C and C1 overlap, indicating that the reduction of bismuth sulfide film occurs simultaneously with that of Ni^{2+} ions.

In the case of sulfate solution, the cathodic peak C1 of reduction of bismuth sulfide film in the background solution is at more negative potential values (Fig. 2, a, cathodic peak C1, –0.55 V) than that (Fig. 1, a, cathodic peak C, –0.3 V) in the nickel-plating solution.
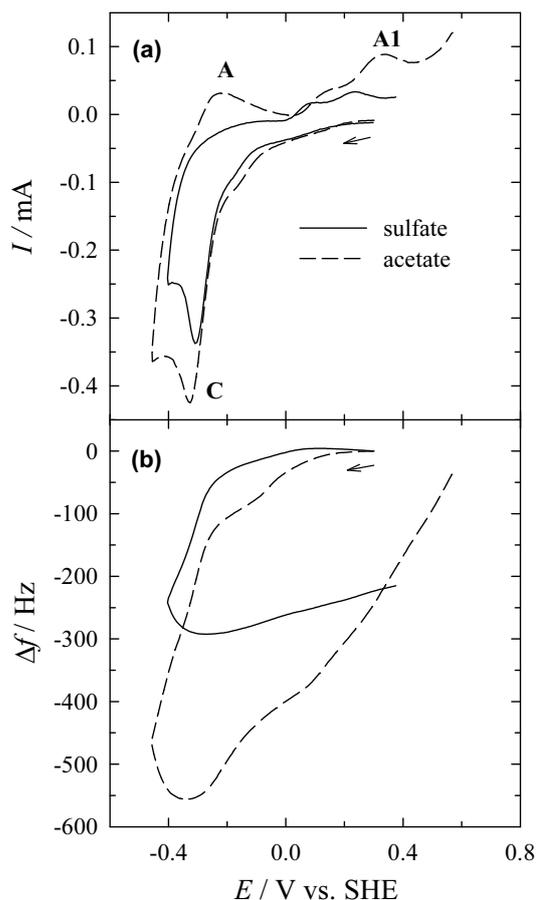
Fig. 1. CVs for current (a) and frequency changes (b) measured on Au modified with bismuth sulfide ($N = 2$) in the 0.05 M NiSO$_4$, 0.32 M H$_3$BO$_3$ (solid line) and 0.05 M Ni(CH$_3$COO)$_2$, 0.32 M H$_3$BO$_3$ (dashed line) solution at pH 4. The potential sweep rate 5 mV s^{-1}; 20 °C
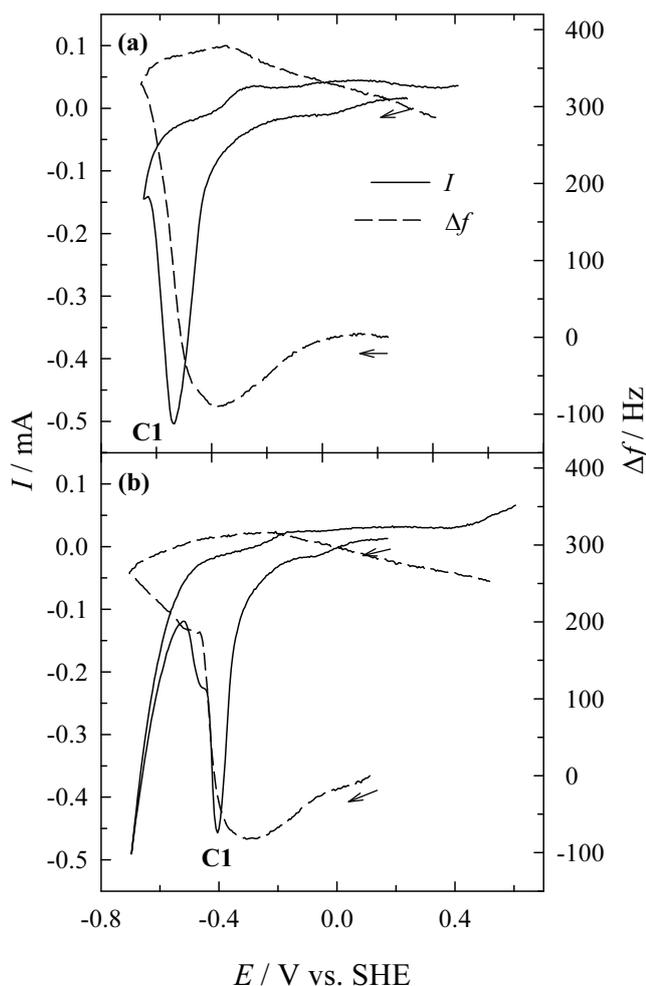
Fig. 2. CVs for current (solid line) and frequency changes (dashed line) measured on Au modified with bismuth sulfide ($N = 2$) in the 0.05 M Na_2SO_4, 0.32 M H_3BO_3 (a) and 0.05 M $Na(CH_3COO)$, 0.32 M H_3BO_3 (b) solution at pH 4. The potential sweep rate 5 mV s^{-1}; 20 °C [23]

As seen in Fig. 1, while cathodic peaks C in both cases are under the same potential region, greater cathodic current and mass changes (Δf) are observed in the solution containing acetate anions as compared to those in the solution containing sulfate anions. It may be suggested that when the film is reduced in the acetate nickel-plating solution simultaneously occurring reduction of bismuth sulfide film offers more active sites for nucleation of Ni before the OPD of it and as evidenced in Fig. 1, higher values of current and mass changes are obtained. Accordingly, the reduction of Ni^{2+} prior to OPD of Ni is more intensive in the Ni plating solution containing acetate anion.

The anodic processes observed after the film reduction also depend on the nature of anion. In the case of acetate Ni plating solution, in the reverse scan anodic peak A is more pronounced. This anodic peak A is related to the oxidation of Ni, which was previously reduced during the cathodic scan (cathodic peak C, Fig. 1, b) [4]. As was determined in [3], the oxidation of film, which was previously reduced in the background solution, occurs at potentials $E > 0.4$ V, the observed anodic peaks under the

potential region from –0.3 V to 0.4 V corresponded to Ni dissolution (Fig. 1, a).

The data of XPS analysis of bismuth sulfide films reduced in the Ni plating solution containing sulfate and acetate anions is shown in Table 1 (samples a and b) and Fig. 3, respectively. According to the XPS data in Table 1 and Ni2p$_{3/2}$ spectra (Fig. 3, d, h), after the reduction of films in both the sulfate and acetate Ni plating solutions, >32 at.% Ni was detected in the film at a depth of 2 nm along with Bi, S and O.

As seen from the Ni2p$_{3/2}$ spectra (Fig. 3, d, h), predominant peaks are observed at $E_b = 852.8$ eV and 852.7 eV, in the case of sulfate and acetate Ni plating solutions, respectively.
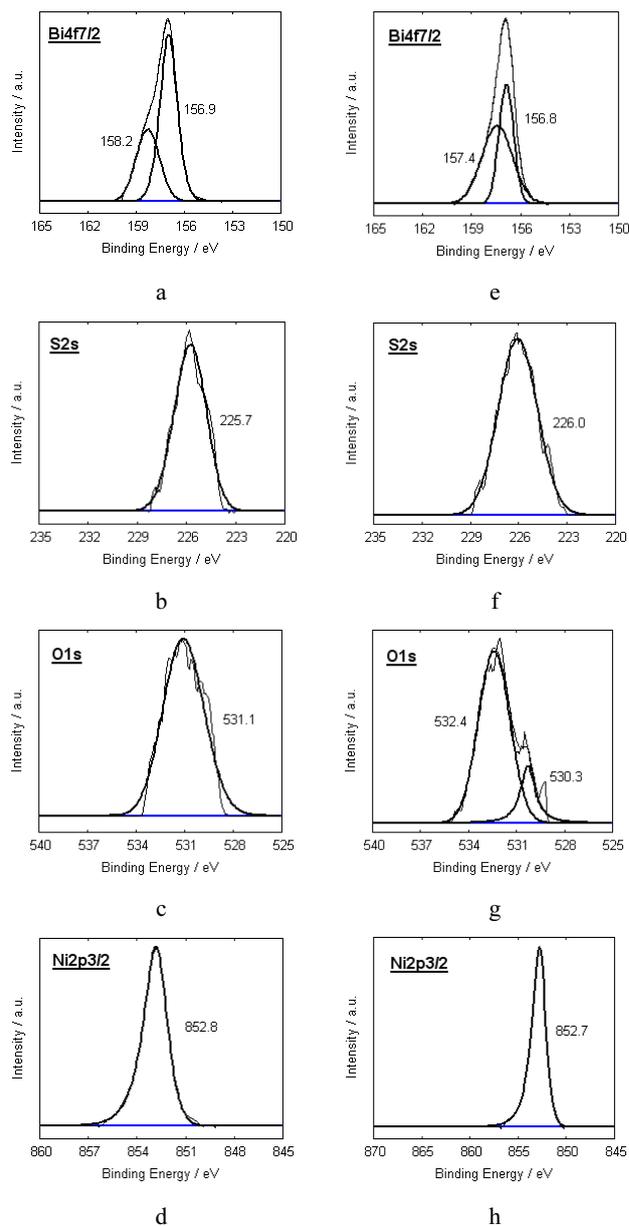
Fig. 3. XPS spectra of Bi4f$_{7/2}$, S2s, O1s and Ni2p$_{3/2}$ for Au modified with bismuth sulfide ($N = 2$) after the cathodic reduction in the Ni^{2+}-containing solution with sulfate (a–d) and acetate (e–h) ions at pH 4. The cathodic potential limit –0.4 V. XPS spectra presented for films at a depth of ~2 nm

Table 1. XPS analysis of the elemental composition of Au electrode modified with bismuth sulfide ($N = 2$) after cathodic reduction in the nickel plating solution with sulfate (a) and acetate anions (b) at pH 4. The cathodic potential limit –0.4 V. The data presented for films at a depth of ~2 nm

Element	Composition (at.%)	E_b (eV)	Bi/S
a) after reduction of bismuth sulfide in the Ni^{2+} containing solution with sulfate anion			
Bi	14.01 and 7.97	156.9 and 158.2	
S	27.37	225.7	
O	18.75	531.1	0.8
Ni	31.91	852.8	
b) after reduction of bismuth sulfide in the Ni^{2+} containing solution with acetate anion			
Bi	8.36 and 11.5	156.8 and 157.4	
S	27.39	226.0	
O	3.11 and 15.59	530.3 and 532.4	0.7
Ni	34.06	852.7	

According to the available literature, the values of E_b for metallic Ni vary in a rather wide interval from 852.2 eV to 853.8 eV [21, 23, 24]. The values of E_b = 852.8 eV and 852.7 eV, established in our study, are close to those mentioned above. Consequently, these values of E_b are attributed to metallic Ni. According to the data in Table 1 and Fig. 3, it may be concluded that the electrode mass increase under the potential region of cathodic peak C is conditioned by the Ni^{2+} incorporation into the bismuth sulfide film and the following reduction to metallic Ni. It also indicates the unchanged stoichiometric ratio of Bi/S after the reduction of film (Table 1).

CONCLUSIONS

It has been determined that the reduction of bismuth sulfide film in the nickel plating electrolyte depends on the anion nature: greater cathodic current and mass changes (Δf) are observed in the solution containing acetate anions as compared to those in the solution containing sulfate anions. As the reduction of bismuth sulfide film in the background solutions depends on the nature of anion, it influences the cathodic reduction of Ni^{2+} ions prior to OPD of Ni. A greater current and mass change (Δf) is conditioned by simultaneously occurring reduction of bismuth sulfide film when the film is reduced in the acetate nickel plating electrolyte in contrast to that in the sulfate one.

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