A study of copper sulfide films by electrochemical quartz crystal microgravimetry

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Thin films of non-stoichiometric copper sulfide $Cu_{2-x}S$ were deposited on Au by SILAR (Successive Ionic Layer Adsorption and Reaction) method and studied by cyclic voltammetry and electrochemical quartz crystal microgravimetry (EQCM). In 0.05 M H_2SO_4, EQCM data showed a qualitative agreement with the attribution of cathodic and anodic currents to sulfur reduction and Cu(I) sulfide oxidation but indicated a participation of additional processes. In 0.1 M NaOH, the existing interpretation of electrochemical processes contradicts the EQCM results; a process resulting in a large mass build-up was found to occur at cathodic reduction of sulfide films alongside with the reduction of sulfur and Cu sulfides.

Key words: copper sulfide films, electrochemical quartz crystal microgravimetry, SILAR method

INTRODUCTION

Copper sulfide films containing non-stoichiometric sulfide $Cu_{2-x}S$ have been used in the last two decades for surface modification of plastics [1–3]; one of important electro-conductive copper sulfide applications was direct electroplating of plastics.

For copper sulfide film characterization, among other methods, the electrochemical techniques such as chronopotentiometry [4, 5] and cyclic voltammetry [6–8] have been successfully used. Copper and glassy carbon substrates were used in these studies, glassy carbon being the most convenient inert electrode providing the widest potential range. The observed electrochemical response was attributed to the cathodic reduction of the sulfide film components (copper sulfides and sulfur) and the subsequent anodic oxidation of the reduction products. Cyclic voltammetry was used also for characterization of the modified copper sulfide [9] and cobalt sulfide layers [10–12].

Identification of electrochemical processes in metal sulfide films may present some problems, with uncertainties in the interpretation of the electrochemical data. Electrochemical quartz crystal microgravimetry (EQCM), giving information on mass changes alongside electrochemical data, may help in a more precise characterization of metal sulfide layers. Recently the EQCM method has been used for investigating Zn selenide film growth in a chemical

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bath [13] and the electrochemical preparation process of Cu_2S layers [14].

In this work, the EQCM technique was applied to copper sulfide films to evaluate the possibilities of this method in studying metal sulfide layers formed by the method known as SILAR (Successive Ionic Layer Adsorption and Reaction).

EXPERIMENTAL

Copper sulfide layers were formed by the SILAR method. In the first step, the substrate being coated was treated for 30 s with copper–ammonia complex solution (the solution contained 0.4 M $CuSO_4 \cdot 5H_2O$, 0.4 M $(NH_2OH)_2 \cdot H_2SO_4$ and NH_3, pH $\approx$ 11; hydroxylamine was added to form copper(I) species) at 20 °C, and rinsed with water. During rinsing, the Cu(II) and Cu(I) complexes in the solution film at the substrate surface are hydrolyzed to insoluble compounds remaining on the substrate. In the second step, the surface was treated with sodium polysulfide solution (0.04 M Na_2S_4) at 20 °C for 30 s and rinsed with water. To obtain a thicker film the procedure was repeated.

EQCM measurements were carried out using AT-cut quartz crystals of 6 MHz fundamental frequency (from Intelemetrics Ltd., UK) sputtered with gold (geometric area 0.636 cm²). Quartz crystals were installed at the bottom of the cell with a working volume of *ca*. 2 ml. The upper part of the cell contained the Pt-wire counter electrode, joints for the electrolyte inlet and the Luggin capillaries, and the

electrolyte outlet tube. EQCM measurements were carried out under stopped-flow conditions. The solutions used were 0.05 M H_2SO_4 and 0.1 M NaOH; before measurements, they were purged with Ar.

EQCM measurements were carried out using a precision frequency counter (43–64) and two digital voltmeters (B7-46/1) connected to a PC through an IEEE 488 interface. A programming potentiostat (PI-50-1) and a sweep generator (PR-8) were used. The measured electrode potential, the faradaic current and the frequency (the stability ± 0.5 Hz) were entered to the PC every 1.3 s. Differential EQCM data (the frequency change rate df / dt) were found as the difference between two frequency measurements per 1 s.

The potential sweep rate was 5 mV s^{-1}, the potential was measured with respect to the Ag / AgCl / KCl$_{sat}$ reference electrode, and its values are given *vs.* the standard hydrogen electrode.

A calibration constant of 7.8 ± 0.4 ng / Hz was found from the electric charge and quartz crystal frequency data of copper dissolution in 0.05 M H_2SO_4 solution (Fig. 1). The copper layer was deposited from the standard acid copper electroplating solution. The calibration constant value was practically equal to that calculated from Sauerbrey's equation.

RESULTS AND DISCUSSION

H_2SO_4 solution. The open-circuit potential of copper sulfide film in 0.05 M H_2SO_4 solution is *ca.* 0.4 V. At a negative potential scan, the cathodic current appears at *ca.* 0.1 V, and a rather sharp current maximum is observed at 0 V (Fig. 2a); the scan was limited to –0.3 V because of hydrogen evolution at more negative potential values. At the subsequent positive potential scan, the anodic current was observed only at potentials more positive than 0.4 V, and the anodic current with no well expressed maximum continued up to 0.85 V. At the second potential scan (dashed curve in Fig. 2), the voltammogram is of a similar form, only the current values are considerably lower and the cathodic current maximum is shifted slightly to more negative potentials.

Figures. 2–4 demonstrate the typical examples of electrochemical and quartz oscillator response of copper sulfide films at a cyclic potential scan. Films in all these experiments were formed by the same procedure, but the film composition could vary considerably in some cases, as is shown by the voltammetric and frequency curves. Apparently, the SILAR procedure including poorly controlled hydrolysis and adsorption steps at irregular solution flow conditions does not ensure strictly reproducible results. The voltammograms in Figs. 2–4, the current maximums K_1 and A_1 may differ both in form and current
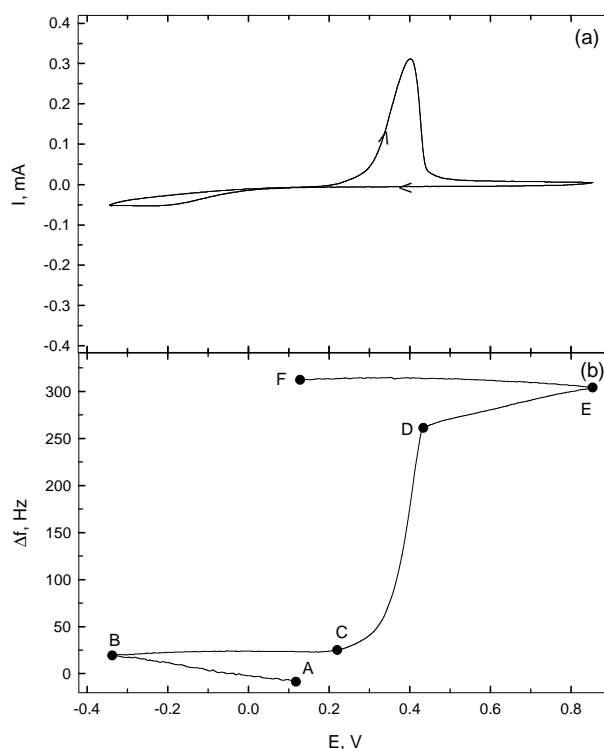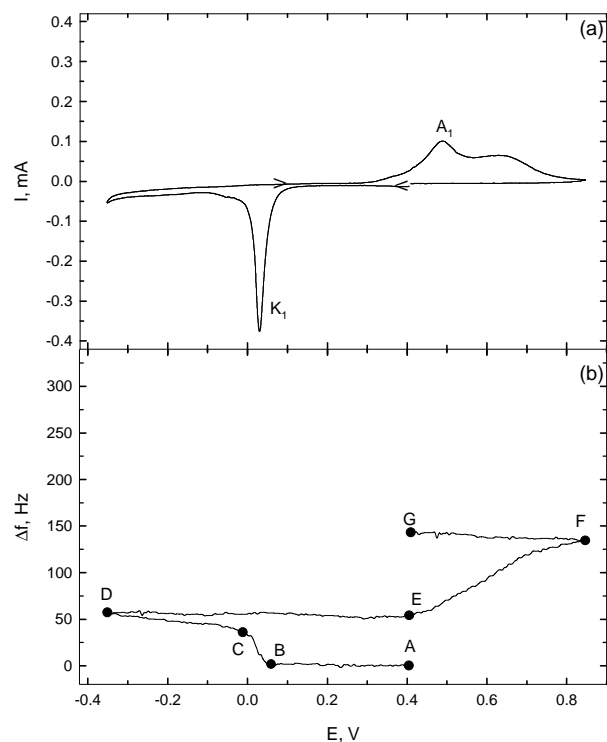

Fig. 1. Cyclic voltammogram (*a*) and simultaneous quartz crystal integral frequency change curve (*b*) recorded in 0.05 M H_2SO_4 solution for Cu film formed on Au electrode by electroplating from the standard acid bath. In Figs. 1–6 potential sweep rate v = 50 mV/s, t^0 = 20 °C
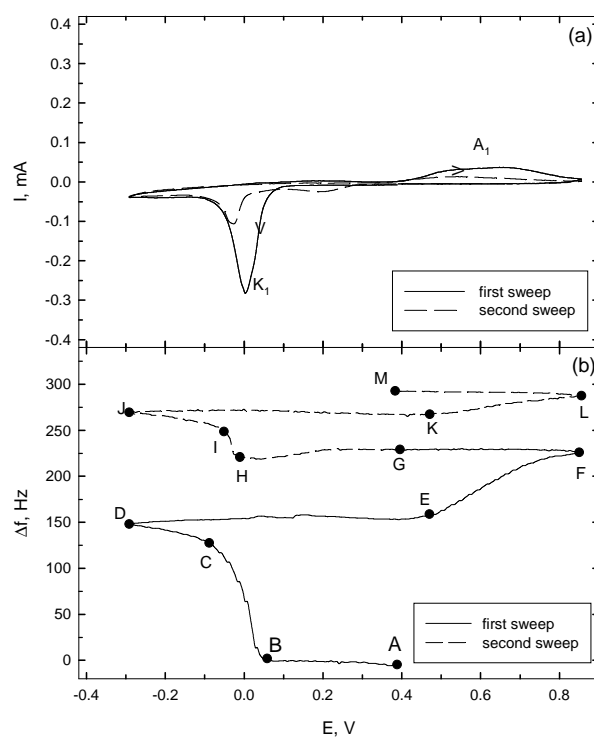
Fig. 2. Cyclic voltammograms (*a*) and simultaneous quartz crystal integral frequency change curves (*b*) recorded in 0.05 M H_2SO_4 solution for Cu sulfide film formed on Au electrode by double SILAR procedure
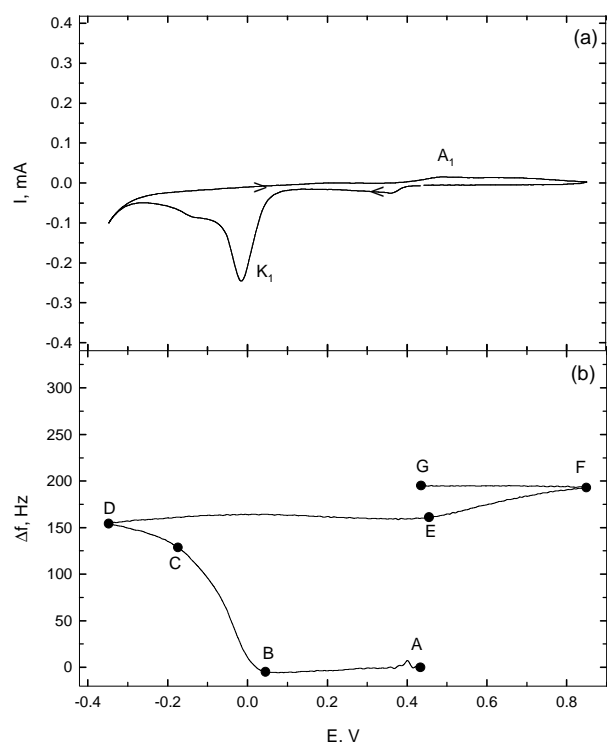
Fig. 3. Cyclic voltammograms (*a*) and simultaneous quartz crystal integral frequency change curves (*b*) recorded in 0.05 M H$_2$SO$_4$ solution for Cu sulfide film formed on Au electrode by double SILAR procedure

Fig. 4. Cyclic voltammograms (*a*) and simultaneous quartz crystal integral frequency change curves (*b*) recorded in 0.05 M H$_2$SO$_4$ solution for Cu sulfide film formed on Au electrode by double SILAR procedure

value. The maximum A$_1$ in some cases splits into two maximums (Fig. 4), and the maximum K$_1$ may become highly asymmetric: additional current is observed at the negative potential side (Fig. 3), indicating the a probability of more than one electrochemical reaction taking place in both cathodic and anodic regions.

The quartz oscillator frequency at the cyclic potential scan either remains practically constant (potential ranges AB, DE and GH in Figs. 2b–4b) or increases (potential ranges BD and EG). The frequency change occurs in the potential regions of currents maximums, implying that the occurring electrochemical processes leads to electrode mass loss.

According to [7], the cathodic current peak K$_1$ represents elemental sulfur reduction to soluble sulfide:

$$S + 2H^+ + 2e \rightarrow H_2S. \qquad (1)$$
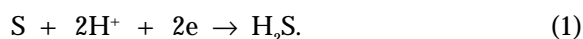
In this reaction, for 1F of charge transferred 0.5 mol sulfur is dissolved (approx. 0.16 mg/1C). The standard potential value of reaction (1), 0.14 V, does not contradict attributing the current peak K$_1$ to sulfur reduction; the situation is less clear with the cathodic current observed in some experiments just after peak K$_1$ (Fig. 3).

Copper sulfide reduction should occur at more negative potentials: the standard potentials of the reactions

$$CuS + 2H^+ + 2e \rightarrow Cu + H_2S \qquad (2)$$

and

$$Cu_2S + 2H^+ + 2e \rightarrow 2Cu + H_2S \qquad (3)$$
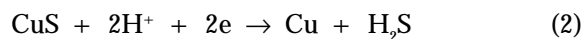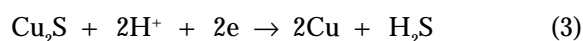
are –0.133 and –0.302 V, respectively. Considering the non-stoichiometric copper sulfide as a mixture of Cu(I) and Cu(II) sulfides, it is possible to explain the cathodic current in the potential region from –0.1 to –0.2 V as a result of reaction (2); the stoichiometric ratio of Cu and S in the sulfide under study is known to be close to 2, therefore the formal, if not real, fraction of CuS should be small and perhaps not well-reproducible, it would correspond to the rather low and not always distinctly seen cathodic current in the potential interval mentioned. On the other hand, in the previous studies [7, 8], the non-stoichiometric copper sulfide reduction peak on glassy carbon was observed at a considerably more negative potential (–0.55 V), and this value was not reached on the Au electrode.

One more possible reaction at cathodic potential scan is Cu(II) sulfide reduction to Cu(I) sulfide:

$$2CuS + 2H^+ + 2e \rightarrow Cu_2S + H_2S, \qquad (4)$$
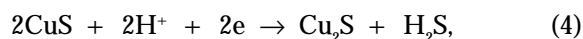
with a standard potential value of 0.036 V. This reaction seems even more

probable than reaction (2) due to a more positive standard potential.

The ratio of mass change to charge transferred in all copper sulfide reduction reactions (2)–(4) is the same as in reaction (1) – approx. 0.16 mg is lost for 1C, in all these cases the electrode mass change occurs on sulfur removal from the electrode surface into solution.

The charge transferred in the peak K_1 area, potential range approx. from 0.1 to –0.1 V, was found to vary from 1.9 to 4.4 mC in various experiments, and the quartz crystal frequency change at the same time (region BC in Figs. 2b–4b was –(45–130) Hz, corresponding to a mass loss of 0.4–1.1 µg. The mass change for 1 C was not constant and changed from 0.15 mg at low values of mass change (Fig. 4) up to 0.26 mg for larger mass changes and charges transferred. Thus, the values of the mass and charge ratio approximately equal to the theoretical one were obtained at a lower electrode surface coverage by the reacting species (most probably sulfur). The enhancement of the experimental mass / charge ratio at higher amounts of reacting species on the surface can be explained by a mechanical removal of some sulfur particles as a result of their diminished adhesion to the electrode surface in the course of reduction reaction and sulfur dissolution occurring at the Au / S interface.

The anodic current in the positive potential region at the subsequent anodic scan (A_1 in Figs. 2a–4a) may be a result of metallic copper dissolution:

$$Cu - 2e \rightarrow Cu^{2+} \tag{5}$$

and / or copper(I) sulfide oxidation to copper(II) species:

$$2Cu_2S - 2e \rightarrow CuS + Cu^{2+} \tag{6}$$
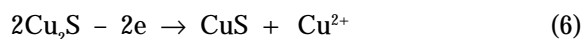
The presence of metallic Cu in the system under study is less probable, since copper sulfide reduction to metallic copper was not reached in the cathodic scan. This was confirmed by special experiments: the cyclic voltammogram of the electrode with electrodeposited Cu shows an anodic current peak in the potential range from 0.2 to 0.4 V (Fig. 1a) and simultaneous quartz crystal frequency rise (Fig. 1b)

The anodic current on the voltammogram of copper sulfide layers is observed at more positive potential values (over 0.4 V), therefore it should be related to reaction (6). The mass change in both anodic processes (5) and (6) results from copper dissolution, and the same ratio of mass decrease and charge transfer should be observed – approx. 0.33 mg/C.

The experimental data on charge and mass change in the potential interval 0.4–0.8 V show a lower mass loss for a unit charge; in most experiments the mass decreased by 0.20–0.26 mg/C. Apparently, alongside the Cu(I) sulfide oxidation reaction (5), some other process accompanied by a lower mass decrease or an opposite mass change takes place. The form of the current maximum in the potential range mentioned supports the idea about two anodic oxidation processes occurring at the overlapping potential regions. A chemical reaction leading to mass build-up can also be involved, *e.g.*, an interaction of Cu^{2+} formed in reaction (5) with sulfide ions remaining at the electrode surface since the cathodic sulfur reduction; this interaction would result in CuS deposit formation and a mass increase compensating to some extent the mass loss in reaction (5).

NaOH solution. In alkaline solutions, the voltammograms of copper sulfide films formed on Au surface are more complicated as compared to those obtained in acid solutions. Two cathodic current peaks at the negative-going potential scan and two anodic current maximums at the positive potential scan are observed (Figs. 5a and 6a). Similar current maximums were obtained in the earlier work [6] for copper sulfide layers on a glassy carbon electrode. The cathodic current in a rather wide potential range, K_1 (peak potential approx. –0.5 V) was attributed to sulfur reduction:

$$S + 2e \rightarrow S^{2-} \tag{7}$$

with E_0 = –0.48 V. The rather sharp current peak K_2 (peak potential in our case approx. –0.96 V) was explained by a reduction of non-stoichiometric Cu sulfide:

$$2Cu_{2-x}S + 2e \rightarrow (2-x)Cu + S^{2-}. \tag{8}$$
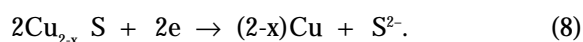
The E_0 values for reduction reactions of CuS and Cu_2S are –0.79 and –0.93 V, respectively. It is necessary to admit the more negative potential values of the both peaks K_1 and K_2 (by approx.0.1 V) on a glassy carbon as compared to Au.

For both reactions (7) and (8), mass loss should be expected at the same ratio as in acid solutions (0.16 mg/C). The quartz crystal frequency data show some mass decrease in the area of peak K_1 (see rising frequency curves BC in Fig. 5c and CD in Fig. 6c). But in the area of peak K_2 a distinct mass build-up was observed (the large frequency fall DE in Fig. 5c and a corresponding very sharp peak in the differential curve in Fig. 5b). Some frequency rise occurs just before and after its fall, the second one being larger (curve EF in Fig. 5c and the corresponding part of the differential curve in Fig. 5b). The picture presented in Fig. 5 is typical of most
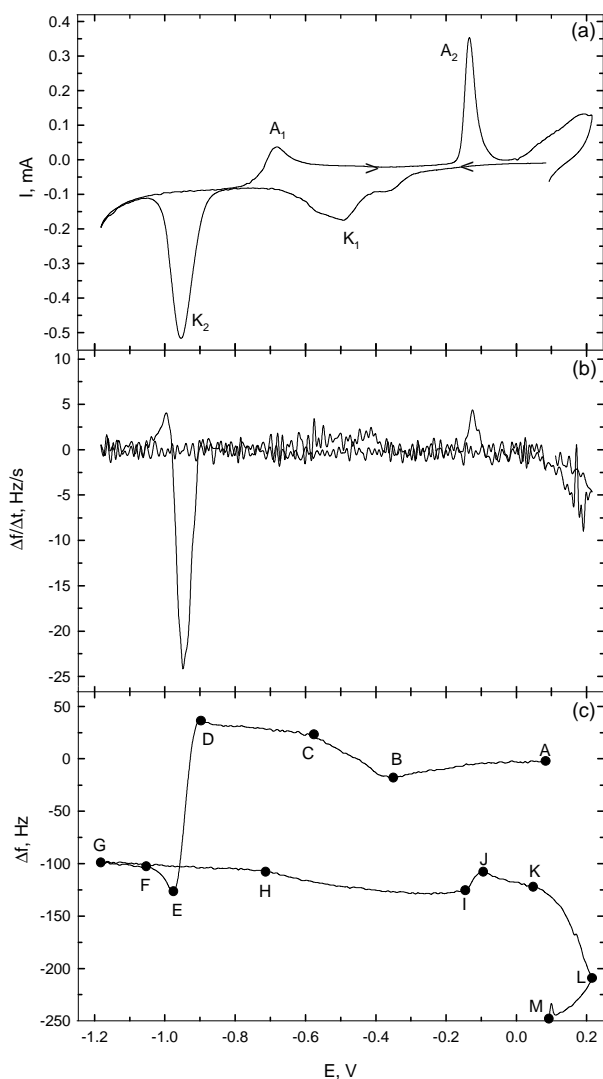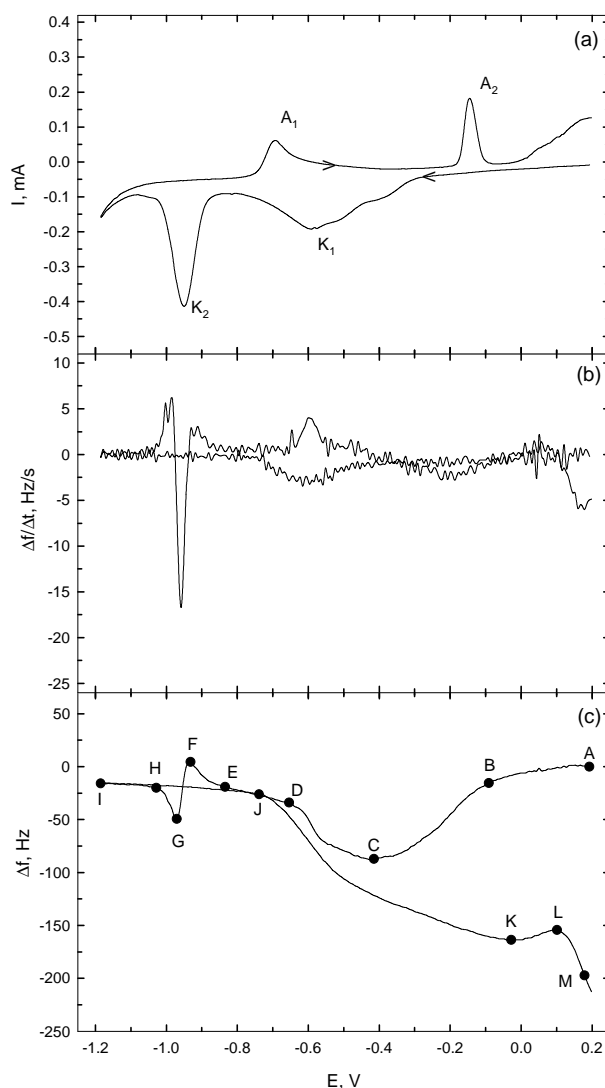
Fig. 5. Cyclic voltammograms (*a*) and simultaneous quartz crystal differential (*b*) and integral (*c*) frequency change curves recorded in 0.1 M NaOH solution for Cu sulfide film formed on Au electrode by double SILAR procedure

Fig. 6. Cyclic voltammograms (*a*) and simultaneous quartz crystal differential (*b*) and integral (*c*) frequency change curves recorded in 0.1 M NaOH solution for Cu sulfide film formed on Au electrode by double SILAR procedure

experiments with copper sulfide films in alkaline solutions. The situation was slightly different in several experiments when no net frequency decrease was found, and the frequency after rising, falling and one more rising returned to the former value (Fig. 6c, EF, FG and GH).

The presented data clearly show that reaction (8) cannot describe adequately the processes in the area of peak K_2. It is evident that two or three consecutive or simultaneous reactions take place in this potential region, the reaction with mass build-up being characterized by the highest mass change rate in this system (see the differential frequency change curves in Figs. 5b and 6b). This process, accompanied by mass increase and connected with reduction reaction, seems to be favoured by OH⁻ ions.

The anodic current peaks A_1 and A_2 are well-reproducible in their potential (–0.67 and –0.14 V,

respectively) and shape, and vary in their height from experiment to experiment. Similar anodic current peaks were observed on glassy carbon [6]; they were attributed to metallic copper sulfidation and oxidation:

$$2Cu + S^{2-} - 2e \rightarrow Cu_2S, \tag{9}$$

$$2Cu + 2OH^- - 2e \rightarrow Cu_2O + H_2O, \tag{10}$$
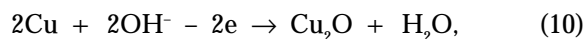
with the corresponding E_0 values: –0.93 and –0.36 V .

The EQCM data for the anodic potential scan are less reproducible and in general are not in agreement with reactions (9) and (10). In the case of reaction (9), the electrode mass should increase by 0.16 mg for 1 C; data for the copper sulfide films in Figs. 5a and 6a give a charge of 1.6 and 2.1 mC for peak A_1, and it should lead to a frequency dec-

rease by approx. 32 and 45 Hz in the potential interval from –0.8 to –0.7 V. Nevertheless, Fig. 5a shows practically no frequency change at these potentials and a little frequency change up to –0.2 V, while in Fig. 6c a continuous frequency decrease in a wide potential range (line JK) is observed. The last frequency change occurs in absence of electrochemical reactions and should be related to some chemical transformation accompanied by electrode mass build-up.

For reaction (10), the mass increase of 0.08 mg/C should be observed. According to Fig. 5a, the charge transferred at the current peak A_2 is 2.8 mC, corresponding to mass gain of 230 ng and frequency decrease by 30 Hz. Instead, the frequency rises by 18 Hz in this potential region (line IJ in Fig. 5c).

The EQCM data demonstrate a complicated character of the processes occurring in cyclic voltammetry experiments with copper sulfide films in alkaline solutions. These processes need further investigations.

CONCLUSIONS

1. EQCM data on electrode mass changes during cyclic voltammetry experiments permit to characterize more precisely the composition and electrochemical behaviour of copper sulfide films.

2. In H_2SO_4 solutions, EQCM is a more suitable method for determination of elemental sulfur in sulfide films as compared to cyclic voltammetry due to a possibility of non-electrochemical removal of sulfur from the surface.

3. At anodic oxidation of sulfide films, the existing reaction scheme does not describe the process adequately and should contain additional reactions.

4. In alkaline solutions, both cathodic and anodic reactions are not confirmed by EQCM data; a process resulting in a large mass build-up was found to occur at cathodic reduction of the sulfide films.

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VARIO SULFIDO DANGØ TYRIMAS ELEKTROCHEMINËS KVARCO KRISTALO MIKROGRAVIMETRIJOS METODU

S a n t r a u k a

Ploni nestechiometrinio vario sulfido $Cu_{2-X}S$ sluoksniai, suformuoti ant Au elektrodo SILAR (konsekutyvinës joniniø sluoksniø adsorbcijos ir reakcijos) metodu, buvo tiriami ciklinës voltamperometrijos ir kvarco kristalo mikrogravimetrijos metodais H_2SO_4 ir NaOH tirpaluose. Elektrodo masës kitimo duomenys, gauti ið kvarco osciliatoriaus daþnio pokyèiø, rûgðèiuose tirpaluose kokybiðkai atitiko esamà reakcijø schemà ir davë informacijos apie papildomus procesus, o ðarminiuose tirpaluose masës kitimo duomenys verèia perþiûrëti visà elektrocheminiø procesø sekà.