

Photoelectrochemical properties of oxide layers formed on sputtered copper coatings in Cu(II) solutions containing ethylenediamine and β -alanine

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Copper layers obtained by magnetron sputtering on glass substrate were exposed to 0.01 M Cu(II) solutions containing 0.005 M ethylenediamine or 0.04 M of β -alanine at pH 5.2 and 6.0, respectively. According to XPS data, non-uniform layers involving cuprous oxide are formed with the absorption coefficient equal to $(5.7\text{--}5.8) \times 10^4 \text{ cm}^{-1}$. When the Cu|solution boundary is excited by the pulses of polychromatic light, oxide layers display the types of conductivity that are opposite to these established for the galvanic copper coatings under the same conditions. Photopotentials and photocurrents also change their sign when the light perturbation is directed to the glass|Cu boundary.

Key words: copper, sputtering, oxides, ethylenediamine, β -alanine, photoresponse

INTRODUCTION

Investigations of oxide layers developed on copper electrodes are interesting from various points of view. They involve various conditions of oxide formation such as heating in air atmosphere, corrosion processes, anodic oxidation, etc. However, there are too many of them to be described here in detailed. We will focus our attention on the layers formed in electrochemical systems containing ligands that are capable of forming various Cu(II) complexes. A spontaneous formation of Cu_2O often attends the electroreduction of Cu(II) and may affect not only the kinetics, but also the mechanism of a charge transfer reaction [1]. Oxide layers developed in such systems are interesting by themselves because their properties may be essentially different from those known for monocrystals or polycrystalline compacts. The latter substances are classified as *p*-type semiconductors and are sensitive to optical perturbation. However, electrochemically formed Cu_2O layers demonstrate not only the common *p*-type behaviour, but often acquire the so-called “anomalous” *n*-type conductivity [2–8]. Various reasons for such effect have been discussed including certain peculiarities of thin layers [9], anion adsorption [10] or deviations from the stoichiometry in oxygen-containing layers [2, 11, 12]. At present, there are no doubts that the properties of oxide layers strongly depend on the conditions under which they are built up. The nature of ligands as well as the composition of ligand-containing solutions is of great importance here. These questions are elucidated in more detail in [13].

This paper deals with further investigations of the main regularities concerning oxide layers spontaneously developed in ligand-containing systems. For this purpose we chose two systems, the properties of which had been studied more exhaustively and which had yielded oxides of different types. These systems were the following:

- Cu|Cu(II), ethylenediamine system with favourable conditions for the formation of *p*- Cu_2O [5, 14, 15], and
 - Cu|Cu(II), β -alanine system, where *n*- Cu_2O is mainly formed [3, 4, 16, 17].
- At the same time, instead of the electrodeposited copper coatings applied in the above investigations, we turned our attention to the copper layers obtained by magnetron sputtering on a glass plate. The main advantage of this technique was that it offered more experimental possibilities due to the transparent (glass) substrate.

EXPERIMENTAL

Copper layers were obtained by magnetron sputtering onto a 1.2 mm thick glass substrate in a device VUP-5M (Ukraine). Commercially available copper of high purity was used for this purpose. The sputtering chamber was evacuated and filled with argon, the pressure of which was maintained at 0.1–0.2 Pa. The temperature in the chamber was about 50 °C. The argon ionisation operated at a voltage of 450 V and a current of 60 mA. The sputtering that lasted 10–20 minutes was enough to obtain 0.3–0.5 μm thick copper layers.

Next, the prepared samples were kept for the controlled time τ in 0.01 M Cu(II) solutions containing 0.3 M K_2SO_4 as a supporting electrolyte and: a) 0.04 M β -alanine (pH 6.0), or b) 0.005 M ethylenediamine

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(pH 5.2). Then photoelectrochemical experiments were carried out in the same solutions. Two types of measurements were employed: a) the investigation of the dynamics of photopotential under open-circuit conditions, and b) the investigation of photocurrents under linear potential sweep conditions. A three-electrode cell with a quartz window was used in the experiments. Electrode potentials were measured with respect to the Ag|AgCl|KCl(sat) reference electrode and were converted to the standard hydrogen scale. Cyclic voltammetric characteristics were recorded at a potential sweep rate of 10 mV s^{-1} using a PI-50-1 potentiostat (Russia). All experiments were performed at $20 \pm 1 \text{ }^\circ\text{C}$.

Two different ways of a chopped optical perturbation from a 150 W halogen lamp were applied. In the first case, the polychromatic light was directed through the quartz window, passed the solution under investigation and fell on the electrode. So, the copper|solution boundary was affected in this case. The power density of polychromatic illumination was controlled by an LM-2 device (Germany) and was estimated to be equal to $\sim 90 \text{ mW cm}^{-2}$. In the other case, the light beam

passed from outside through the glass substrate and perturbed mainly the copper|glass interphase. To assess the absorption coefficient in the Cu_2O layer, the power densities of falling, reflected and outgoing light beams were measured using the LM-2, SiO_2 photodiode, thin glass plates and optical fibers.

More than 15 samples were investigated. The most typical results that reflect the main photoelectrochemical peculiarities of the systems were selected for the presentation below.

X-ray photoelectron spectroscopy (XPS) experiments were performed with an Escalab MK11 spectrometer (United Kingdom) using the samples formed at different immersion times. The source of excitation was a double anode with Mg $K\alpha$ line radiation whose energy was 1253.6 eV and power was 300 W (15 kV , 20 mA). The spectrometer was calibrated against Cu $2p_{3/2}$ at $932.4 \pm 0.1 \text{ eV}$, Ag $3d_{5/2}$ at $368 \pm 0.1 \text{ eV}$ and Au $4f_{7/2}$ at $83.6 \pm 0.1 \text{ eV}$. The pressure in the UHV analyzer chamber was maintained at $1.33 \times 10^{-7} \text{ Pa}$. The spectra for every element were recorded 3–5 times and the data obtained were averaged and compared with the standards [18]. The samples were also etched by ionised argon at a current of $100 \mu\text{A/cm}^2$ that corresponds to an etching rate of $\sim 30 \text{ nm min}^{-1}$.

RESULTS AND DISCUSSION

A typical example of Cu $2p_{3/2}$ spectra for a copper layer obtained by magnetron sputtering is shown in Fig. 1. A single line corresponding to the metallic copper is observed at 932.2 eV for different depths (x) of the layer attaining 450 nm , where at 937.5 eV there appears the extra line. It could be attributed to CuSiO_3 . This means that the surface of the glass substrate is reached when etching the copper layer with Ar^+ ions. These data were used for the estimation of the thickness of the Cu layers formed on the glass plates.

The Auger spectra shown in Fig. 2 were obtained for the copper layers that were kept for 24 hours in the solutions under investigation. It may be seen that a noticeable part of copper is oxidized with the formation

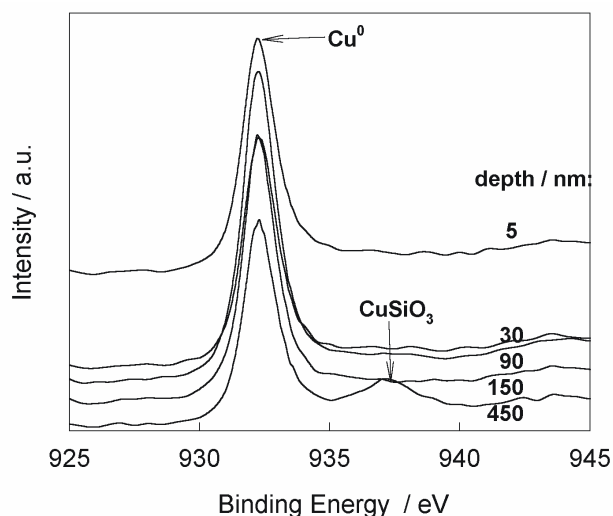


Fig. 1. Cu $2p_{3/2}$ spectra of the sample obtained by magnetron sputtering. The thickness of the surface layer removed with Ar^+ beam is indicated at the respective curves

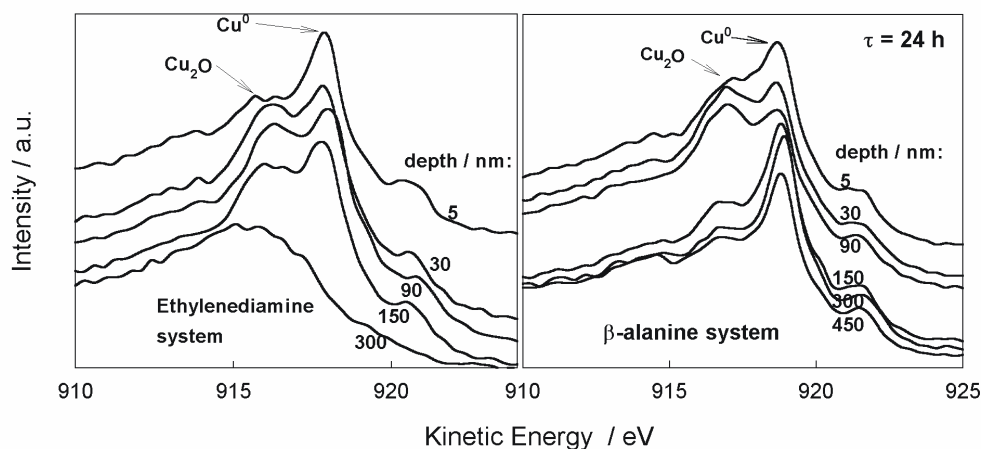


Fig. 2. Auger spectra CuL3M45M45 of Cu samples exposed in the ethylenediamine (left) and β -alanine (right) systems for 24 h. The thickness of the surface layer removed with Ar^+ beam is indicated at the respective curves

of Cu_2O . In the case of ethylenediamine system, the content of Cu_2O is approximately the same at different depths. Cuprous oxide prevails only at the very surface of the glass substrate. A similar picture is also observed for the surface layers in the case of β -alanine system. However, a deeper penetration of oxygen into copper is more inhibited as compared with the previous case. As a result, the metallic copper prevails at $x > 150$ nm.

The absorption ability of the layers was estimated by means of a well-known equation

$$I(x) = I_0 (1 - R) \exp(-\alpha x),$$

where α is the absorption coefficient, $R = I_r / I_0$ is the reflection coefficient, I_0 , I_r and $I(x)$ are the intensities of the applied, reflected and passed light, respectively. The last three quantities were measured as described above. It was obtained that $\alpha = 5.7 \times 10^4 \text{ cm}^{-1}$ for the layers formed in the ethylenediamine system and $\alpha = 5.8 \times 10^4 \text{ cm}^{-1}$ in the case of the β -alanine system. Such α values are typical of semiconductors, where fundamental absorption occurs due to the transfer of electrons from valency to a conductance band. The obtained results show that about half of the optical irradiation is already absorbed in 120 nm thick layer and only 4–7% goes outside.

The equilibrium potential of Cu electrode in the ethylenediamine solution is equal to 0.238 V [6]. However, the observed open-circuit potentials E_{oc} ranging from 0.250 to 0.256 V are higher and, consequently, indicative of oxide formation. The response of this system to light pulses may be seen from Fig. 3. The negative photopotential (E_{ph}) arises when the Cu|solution boundary is excited. The level of the response shows a tendency to increase with the exposure time. A comparison of these data with analogous characteristics obtained in [6] for galvanic coatings shows that: a) E_{oc} for the sputtered coatings is by ~ 10 mV less, b) E_{ph} observed for the sputtered and galvanic coatings have opposite signs, and c) $|E_{\text{ph}}|$ is twice as high when galvanic coatings are used.

The dynamics of the electrode potential is quite otherwise when the optical perturbation is directed towards the glass|Cu boundary. The photoresponse is significantly weaker in this case, but this cannot arise from the light losses in the glass that are less than 8%. The main difference, however, lies in the fact that E_{ph} in some cases (at moderate exposure times) are positive.

Somewhat similar phenomena are observed in the β -alanine system (Fig. 4). The average E_{oc} in this case is ~ 0.265 V and is consistent with data obtained earlier [19]. In contrast with the previous system, positive pho-

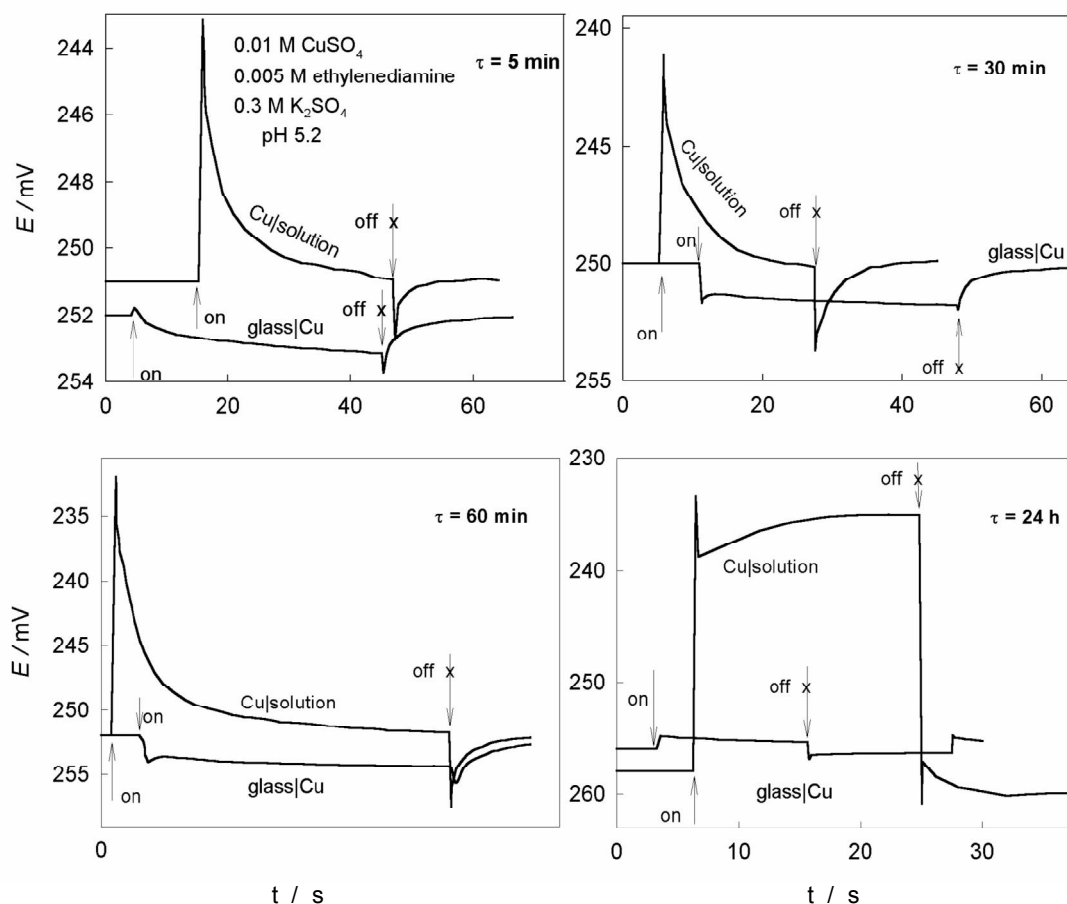


Fig. 3. Response of open-circuit potential E to optical perturbation. Cu electrode was immersed for the indicated time τ into the solution containing 0.01 M Cu(II) 0.005 M ethylenediamine and 0.3 M K_2SO_4 at pH 5.2. The boundary that was exposed to light is also named at the respective curves

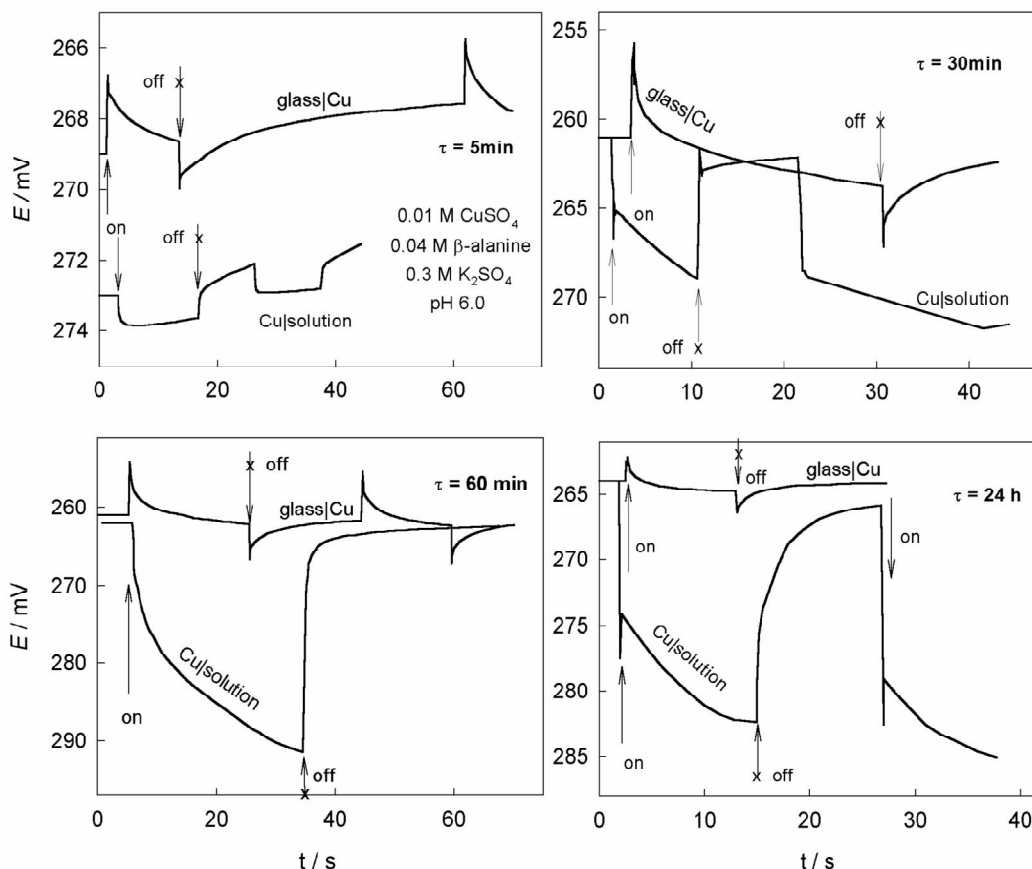


Fig. 4. The same as in Fig. 3 obtained for the β -alanine system

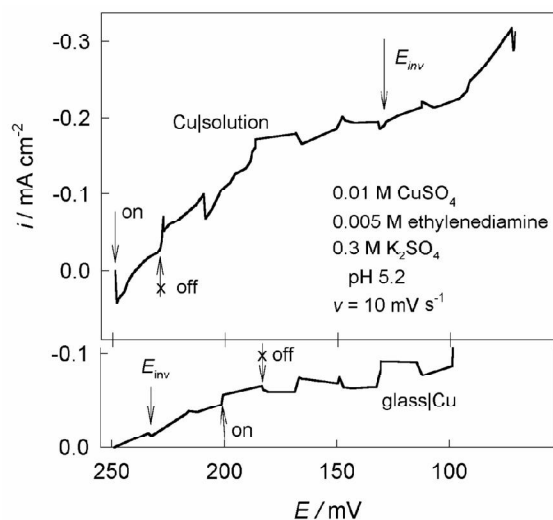


Fig. 5. Voltammograms obtained under chopped illumination conditions for the ethylenediamine system. Exposure time τ 24 h

topotentials are observed when the Cu|solution boundary is excited. Again, E_{ph} for the sputtered and the galvanic coatings [4] have opposite signs and, as described above, E_{ph} changes its sign when the glass|Cu boundary is perturbed.

The potentiodynamic data discussed above are in agreement with the photovoltammetric behaviour of the systems. In the case of the ethylenediamine solutions, the photocurrents (i_{ph}) are not high (Fig. 5). However,

it is possible to detect that i_{ph} are positive (anodic) at low cathodic polarizations. This fact as well as the negative E_{ph} referred above is indicative of n -type conductivity that displays itself when the Cu|solution boundary is excited.

A similar regularity retains for the β -alanine system as well. This can be seen from a comparison of Figs. 4 and 6: negative photocurrents are compatible with positive photopotentials. Hence, the oxide layers formed in this system exhibit p -type conductivity at the Cu|solution boundary.

It is more difficult to ascertain whether this regularity is also valid for the glass|Cu boundary, since the photocurrents are weak in this case. Though negative photocurrents are generated at $E < 0$ (Fig. 6, upper part), it could be stated that they are positive at low cathodic polarizations, since a certain inversion potential (E_{inv}) may be detected at ~ -0.2 V, where i_{ph} changes its sign. Similar effects have been observed earlier for n -Cu₂O developed in the β -alanine system [4], and E_{inv} was treated as a flat-band potential. In the case of semiconducting oxide layers, its position should depend on the solution pH that was actually observed in the experiments [4].

In summary, it seems possible to conclude that the oxides developed on the copper layers obtained by magnetron sputtering exhibit specific photoelectrochemical properties. Moreover, the characteristics of the photo-

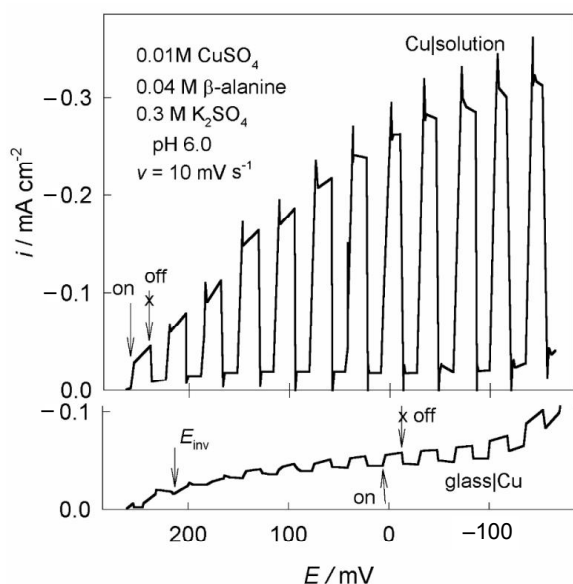


Fig. 6. The same as in Fig. 5 obtained for the β -alanine system

response depend also on which boundary, Cu|solution or glass|Cu, is excited. The latter effect seems to be impossible in the case of homogeneous oxide layers. This phenomenon could be related to a certain extent to a non-uniform distribution of oxygen that is responsible for the deviations from the stoichiometry in the oxygen-containing layers. It is not clear for now, whether the established regularities are universal for these thin irregular layers. To understand the nature of the phenomena occurring in such systems in more detail, further investigations are required.

CONCLUSIONS

1. Non-uniform layers involving cuprous oxide are formed on copper and obtained by magnetron sputtering on a glass substrate when they are exposed to 0.01 M Cu(II) solutions containing ethylenediamine or β -alanine at pH 5.2 and 6.0, respectively.

2. When the Cu|solution boundary is excited by the pulses of polychromatic light, the oxide layers formed in the ethylenediamine and β -alanine systems exhibit n - and p -type conductivities respectively. The signs of the photoresponse are opposite to the ones established for the galvanic copper coatings under the same conditions.

3. Photopotentials and photocurrents change their signs when light perturbation is directed to the glass|Cu boundary. In this case, the type of conductivity is similar to the one established for the galvanic coatings.

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References

1. A. Survila and V. Uksienė, *Electrochim. Acta*, **37**, 745 (1992).

2. B. Pointu, H. Braizaz, P. Poncet and J. Rousseau, *J. Electroanal. Chem.*, **122**, 111 (1981); **151**, 65 (1983).
3. A. Aruchamy and A. Fujishima, *J. Electroanal. Chem.*, **266**, 397 (1989); **272**, 125 (1989).
4. A. Survila, P. Kalinauskas and V. Uksienė, *Electrochim. Acta*, **38**, 2733 (1993).
5. A. Survila, P. Kalinauskas, E. Ivaškevič and W. Kutner, *Electrochim. Acta*, **42**, 2935 (1997).
6. A. Survila, P. Kalinauskas and I. Valsiūnas, *Chemija*, **10**, 275 (1999).
7. A. Survila, P. Kalinauskas and I. Valsiūnas, *Russ. J. Electrochem.*, **38**, 1068 (2002).
8. J. Būdienė, P. Kalinauskas and A. Survila, *Chemija*, **15**, 7 (2004).
9. U. Bertocci, *J. Electrochem. Soc.*, **125**, 1598 (1978).
10. A. Sh. Valeyev, *Elektrokhimiya*, **17**, 1890 (1981).
11. B. Millet, C. Fiaud, C. Hinnen and E. M. M. Sutter, *Corrosion Sci.*, **37**, 1903 (1995).
12. R. Babić, M. Metikoš-Huković and M. Lončar, *Electrochim. Acta*, **44**, 2413 (1999).
13. A. Survila, A. Survilienė, S. Kanapeckaitė, J. Būdienė, P. Kalinauskas, G. Stalnionis and A. Sudavičius, *J. Electroanal. Chem.*, **582**, 221 (2005).
14. A. Survila, A. Survilienė and G. Stalnionis, *Chemija*, **10**, 203 (1999).
15. A. Survilienė and A. Survila, *Russ. J. Electrochem.*, **38**, 1216 (2002).
16. A. Survila, P. Kalinauskas and V. Uksienė, *Chemija*, **1**(180), 154 (1991).
17. A. Survila, P. Kalinauskas and V. Uksienė, *Chemija*, **9**, 51 (1998).
18. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Minnesota (1978).
19. A. Survila and V. Uksienė, *Sov. Electrochem.*, **25**, 856 (1989).

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OKSIDŲ SLUOKSNIŲ, SUFORMUOTŲ CU(II), ETILENDIAMINO IR β -ALANINO TIRPALUOSE ANT UŽDULKINTŲ VARIO DANGŲ, FOTOELEKTROCHEMINĖS SAVYBĖS

Santrauka

Vario dangos, gautos magnetroninio dulkinimo būdu ant stiklo padėklo, buvo eksponuojamos 0,01 M Cu(II) tirpaluose, turinčiuose 0,005 M etilendiamino (pH 5,2) arba 0,04 M β -alanino (pH 6,0). Rentgeno fotoelektroninės spektroskopijos metodu nustatyta, kad šiomis sąlygomis susidaro nevienalyčiai Cu₂O sluoksniai, kuriuose šviesos absorbcijos koeficientas yra lygus $(5,7-5,8) \times 10^4 \text{ cm}^{-1}$. Rezultatai, gauti žadinant vario ir tirpalo sandūrą polichromatinės šviesos impulsais, rodo, kad oksidų laidumas yra priešingo tipo, negu tas, kurį įgyja sluoksniai, suformuoti ant galvaninių dangų tomis pačiomis sąlygomis. Kai žadinanti šviesa yra nukreipta į vario ir stiklo sandūrą, fotopotencialai ir fotosrovės pakeičia savo ženklą.