VILNIUS UNIVERSITY
CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY
INSTITUTE OF CHEMISTRY

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INVESTIGATION OF PECULIARITIES OF COBALT AND ITS ALLOYS ELECTROLESS DEPOSITION

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INTRODUCTION

Co alloy thin films play a major role in development of magnetic devices and microelectromechanical systems. Renewed interest to the Co electroless deposition process is due to the application of the CoP or CoB thin films as barrier layers for protection of Cu layer in microelectronical systems. Though a CoP film was found to be an effective barrier against Cu diffusion, it was proposed that introduction of a third alloying element, especially a refractory metal (W, Mo, Re), may improve the barrier efficiency. An application of ternary Co-based films as diffusion barriers for Cu solves some problems preventing contamination by copper. The solutions for electroless deposition of the CoPW alloys commonly contain citrate ions as a complexing agent. The possibility of the use of glycine as a complexing agent for Co(II) ions in a wide pH range, leading to the deposition of films with different composition and microstructure, was also demonstrated. Glycine serves as a complexing agent as well as a buffering additive.

Boron containing compounds borohydrides or borazanes are stronger reducing agents as compared to sodium hypophosphite. A commonly used boron-containing reducing agent borazane dimethylamine borane (DMAB), enables deposition of the cobalt films at a markedly lower pH (5-9). The advantage of boron-containing reducing agents is the so-called ‘self-activated’ cobalt deposition. This means the beginning of electroless deposition on copper without a prior Pd activation step. Data concerning the use of other boranes for the electroless deposition of metals are scarce. The suitability of morpholine borane for cobalt and nickel deposition is mentioned only in some patents, however, there are no data concerning this process and properties of the coatings obtained. Therefore, it was important to investigate electroless cobalt deposition with morpholine borane as a reducing agent in the solutions containing an alkaline metal-free ligand glycine.

In this study we also present a simple way for preparation of the gold-cobalt and gold-cobalt-boron catalysts with low Au loadings deposited on the copper surface. The electrocatalytic activity of the mentioned catalysts towards the oxidation of BH_4^- ions is compared with that of bare Au, Co/Cu and CoB/Cu electrodes.

The aim of the work was to investigate the peculiarities of electroless deposition of cobalt coatings in the glycine solutions using sodium hypophosphite and morpholine borane as reducing agents, as well as to determine the composition of the coatings obtained and the possibilities of their employment for the formation of barrier layers on copper and application for fuel cells production.

The main tasks of the work were as follows:

1. It is possible to deposit high-quality CoWP in glycinate solution using sodium hypophosphite as a reducing agent. The coatings contain up to 5 at. % of W and up to 6,3 at. % of P.
2. The CoWP coatings deposited using sodium hypophosphite as a reducing agent are a suitable barrier layer, capable to protect from copper substrate diffusion.
3. At a relatively low temperature of 30 ^{o}C it is possible to obtain a wide variety of coatings from nearly pure Co coatings to CoB alloys containing up to 13 at. % B when using morpholine borane as a reducing agent and selecting appropriate conditions.
4. The cobalt coatings, electrolessly deposited using morpholine borane as a reducing agent and further coated with the gold crystallites, are suitable catalysts for the electro-oxidation of sodium borohydride.

Novelty and actuality of the work

Electroless deposition of the CoWP coatings using glycine as a ligand was performed for the first time. It has been found that it is possible to deposit high-quality CoP and CoWP coatings from the glycine-containing solutions using sodium hypophosphite as a reducing agent. It was shown that the electrolessly deposited cobalt coatings containing tungsten are a suitable barrier layer capable to protect from copper substrate diffusion.

Electroless deposition of the cobalt coatings using morpholine borane as a reducing agent has not been studied previously and was performed in the present study. After deposition conditions had been selected, nearly pure Co coatings and CoB alloys containing up to 13 at. % of boron were deposited.

It was shown that the cobalt or cobalt-boron ad-layers coated with the gold particles are promising catalysts and can be used in direct borohydride fuel cells.

2. EXPERIMENTAL

2.1. Chemicals and solutions

The solutions were prepared from Alfa Aesar, Sigma-Aldrich, Chempur and Eurochemicals analytical grade reagents. Three times distilled water was used to prepare all the solutions. Measurements of pH were achieved using EV - 74 pH - meter and a ESL 43-07 glass electrode. Solution pH was adjusted with NaOH or $(CH_3)_4N(OH)$ (tetramethylammoniumhydroxide).

2.2 Electroless deposition of the cobalt films

Electroless deposition of the CoP and CoWP films was performed on a copper foil or copper deposited by sputtering on silicon wafers with thermal SiO_2 covered by Ta (Cu 100 nm/Ta 25 nm/SiO_2/Si) (for investigation of microstructure and barrier properties of the films) without activation with Pd(II) ions. After cleaning and rinsing, the Cu substrate was immersed in the solution containing 0.5 mol l^{-1} $NaBH_4$ and 0.5 mol l^{-1} NaOH at 50 - 60 ^{o}C for 5 min, then rinsed with distilled water and dipped into the electroless cobalt plating solution, the main composition of which was as follows (mol l^{-1}): $CoSO_4$ - 0.1, NH_2CH_2COOH (glycine) - 0.6, NaH_2PO_2 - 0.5 (if not pointed otherwise), an additional buffering agent - (0 - 0.5) and Na_2WO_4 - (0 - 0.2). The buffering agent used was one of the listed dicarboxylic acids (malonic, succinic, adipic, tartaric) or orthoboric acid. The deposition of films was performed always from a freshly prepared solution at a temperature of 80 ^{o}C.

Electroless deposition of the Co-B films was performed on the mentioned above copper surface. The main composition of solutions was as follows (mol l^{-1}): $CoSO_4$ - 0.05, NH_2CH_2COOH (glycine) - 0.1; $C_4H_8ONH{\cdot}BH_3$ (morpholine borane, MB) - 0.05. The deposition of films was performed from a freshly prepared solution at a temperature of 30 ^{o}C.

2.3. Fabrication of the Au/Co/Cu and Au/CoB/Cu catalysts

Au nanoparticles were deposited on the Co/Cu and CoB/Cu electrodes by galvanic displacement of gold from a 5 mmol l^{-1} $KAu(CN)_2$ + 0.4 mol l^{-1} $(NH_4)_2C_6H_6O_7$ complex (pH 5.0) (denoted as the neutral $KAu(CN)_2$ solution) at 30 °C or from a 1 mmol l^{-1}

$HAuCl_4$ solution (pH 1.8) (denoted as the acidic $HAuCl_4$ solution) at 25 °C. The immersion time periods of the Co/Cu or CoB/Cu electrodes into the both gold-containing solutions were 0.5, 1 and 5 min. The fabricated catalysts were used for borohydride electro-oxidation measurements without any further treatment.

2.4. Instruments and methods

The thickness of deposited films was determined gravimetrically. The composition of the films obtained was determined by means of X-ray photoelectron spectroscopy (XPS) using an 'ESCALAB MKII' spectrometer (VG Scientific, Great Britain) using X-radiation of Al Kα (1486.6 eV, pass energy of 20 eV). A pressure of $1.33 \cdot 10^{-6}$ Pa was maintained in the UHV analysis chamber. The samples were etched in the preparation chamber by ionized argon at a vacuum of $5 \cdot 10^{-4}$ Pa to 40 nm with the purpose of eliminating errors due to surface oxidation. The accelerating voltage of ca. 4.0 kV and a beam current of 100 μA cm^{-2} were used, which corresponded to an etching rate of ca. 20 nm min^{-1}. The $Co2p_{3/2}$, $Cu2p_{3/2}$, W4f, P2p, B1s and O1s spectra were recorded to determine the elemental composition of the coatings. The quantities of Co, W, P, B and O were expressed in at. %. The standard deviation for the method was estimated to be 0.1 - 0.5 at. %.

The morphology of the CoP and CoWP films and roughness of the surface R_{RMS} (root mean square roughness) were investigated by means of contact mode AFM on a scanning probe microscope Explorer (Thermomicroscopes, USA).

The morphology and composition of the Au/Co/Cu and Au/CoB/Cu catalysts were characterized using a SEM/FIB workstation Helios Nanolab 650 with an energy dispersive X-ray (EDX) spectrometer INCA Energy 350 X-Max 20. The Au metal loading was estimated from EDX data using Thin Film ID software.

XRD patterns of CoP and CoWP were measured using an X-ray diffractometer D8 from Bruker AXS. Cu Kα radiation with a primary beam monochromatization and parallel beam optics was used. XRD patterns were measured in a conventional θ:θ mode and using the method of grazing incidence. In the latter case the angle between the primary beam and sample surface equaled 0.5°. Patterns were measured in 2θ range from 30 to 80° in a step scan mode with a step size of 0.04° and a counting time of 6 s.

XRD patterns of Au/Co/Cu were measured using an X-ray diffractometer SmartLab (Rigaku) equipped with a 9 kW X-ray tube with a rotating Cu anode. The grazing incidence (GIXRD) method was used in the 2Θ range of 30 - 85°. The angle between the parallel beam of X-rays and the specimen surface (ω angle) was adjusted to 0.5°.

2.5. Electrochemical measurements

A conventional three-electrode electrochemical cell was used for electrochemical measurements of borohydride oxidation. The as-prepared Co/Cu, CoB/Cu, Au/Co/Cu and Au/CoB/Cu catalysts with a geometric area of 2 cm^2 were employed as working electrodes, an $Ag/AgCl/KCl_{sat}$ electrode was used as a reference and a Pt sheet was used as a counter electrode. An Au-sputtered quartz crystal with a geometric area of 0.636 cm^2 was used as a bare gold electrode. The presented current densities are normalized with respect to the geometric area of catalysts.

All electrochemical measurements were performed with a Zennium electrochemical workstation (ZAHNER-Elektrik GmbH & Co.KG). Steady state linear sweep voltammograms were recorded at a potential sweep rate of 10 mV s^{-1} from the stationary E_s value in the anodic direction up to 0.8 V in a 1 mol l^{-1} NaOH solution containing 0.05 mol l^{-1} $NaBH_4$ at 25 ^{o}C. The electrode potential is quoted *versus* the standard hydrogen electrode (SHE).

The chronoamperometric measurements were carried out by, at first, holding the potential at open circuit for 10 s, and then stepping to -0.9 and 0 V, respectively, for 2 min.

3. RESULTS AND DISCUSSION

3.1. CoP and CoWP films deposited using sodium hypophosphite

Electroless cobalt alloy deposition solutions containing glycine as a ligand and sodium hypophosphite as a reducing agent are stable enough and may be used for deposition of the CoP films without additional additives. The rate of films deposition rises markedly with increase in temperature and solution pH. By changing solution pH

and using the buffering H_3BO_3 additive, the amount of the incorporated P can be varied in the range from ca. 4.5 to 6.3 at. %.

Dicarboxylic acids have an accelerating effect similar to that of boric acid on the rate of cobalt alloy deposition from the glycine-containing solutions. The deposition rate of CoP coatings and amount of incorporated phosphorus increase continuously with increase in succinic acid concentration (Fig. 1). Moreover, with increase in succinic acid concentration the change in solutions pH after deposition of the same amount of the CoP coating decreases, indicating some improvement in buffering capacity of the solution.

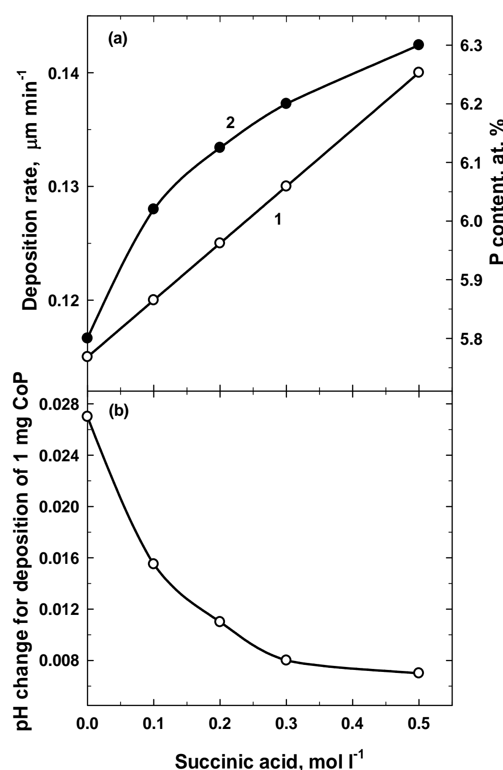
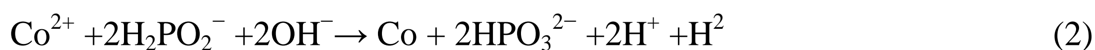


Fig. 1. (a) Dependence of the CoP deposition rate (1) and P content in the films (2) on concentration of succinic acid and (b) alteration of pH for deposition of 1 mg CoP on concentration of succinic acid. Composition of solutions (mol l^{-1}): $CoSO_4$ – 0.1, NH_2CH_2COOH – 0.6, NaH_2PO_2 – 0.5; pH 10.

Such an action of buffering additives can be clarified when considering possible reactions proceeding in the oxidation of sodium hypophosphite in an alkaline medium, wherein OH^- ions react with a hypophosphite oxidation product $H_2PO_3^-$ forming the end-product of HPO_3^{2-} according to Eq. 1:

$$H_2PO_3^- + OH^- \rightarrow HPO_3^{2-} + H_2O \qquad (1)$$

The overall process of electroless deposition of cobalt in an alkaline medium can be expressed by the following reactions:



$$Co^{2+} + 2H_2PO_2^{-} + 2OH^{-} \rightarrow Co + 2HPO_3^{2-} + 2H^{+} + H^{2} \quad (2)$$

$$2H_2PO_2^{-} \rightarrow P + HPO_3^{2-} + 1/2H_2 + H_2O \quad (3)$$

$$H_2PO_2^{-} + OH^{-} \rightarrow HPO_3^{2-} + H_2 \quad (4)$$

It is obvious, that OH^{-} ions are consumed during the overall process of the cobalt alloy formation and solution pH is decreased. Generally, a drop in solution pH results in the decrease in the electroless plating rate. In our case succinic acid acts as a buffering substance and at sufficient concentrations does not allow solution pH to decrease dramatically and thus accelerates the plating rate. It has been found that other dicarboxylic acids: malonic, adipic and tartaric, used in the glycine-containing solution, act similarly to succinic acid. An improvement of the solution buffering capacity and accelerating effect on cobalt deposition rate increase with an increase $-CH_2-$ groups in the molecule of dicarboxylic acid (Table 1).

Table 1. Parameters of CoP and CoWP deposition and composition of obtained films. Composition of solutions (mol l^{-1}): $CoSO_4$ – 0.1, NH_2CH_2COOH – 0.6, NaH_2PO_2 – 0.5, buffering additive – 0.3, pH 10.

Buffering acid	Na_2WO_4, mol l^{-1}	Deposition rate, µm min^{-1}	ΔpH for deposition of 1 mg of coating	Films composition, at.%		
				Co	W	P
none	-	0.105	0.031	95.9	-	4.1
malonic	-	0.115	0.015	93.9	-	6.1
succinic	-	0.118	0.012	93.7	-	6.3
adipic	-	0.150	0.007	93.5	-	6.5
tartaric	-	0.113	0.010	93.7	-	6.3
none	0.05	0.075	0.035	93.8	3.3	3.1
malonic	0.05	0.080	0.016	92.2	4.4	2.9
succinic	0.05	0.085	0.014	91.7	4.2	3.1
adipic	0.05	0.075	0.010	91.7	4.8	3.5
tartaric	0.05	0.070	0.015	91.5	4.3	4.2

Deposition rate of the cobalt alloy decreases even if 0.01 mol l^{-1} of Na_2WO_4 is added to the solution of electroless deposition. In this case the decrease in the amount of P in the films (about to 2 at. %) is significant in the whole investigated pH range from 8 up to 11. The amount of W in the films decreases with increase in solution pH, whereas the amount of P increases, so the amounts of P and W in the cobalt films change in

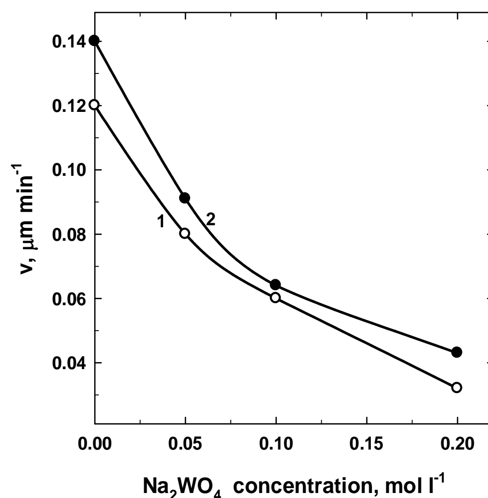


Fig. 2. Dependence of the CoWP films deposition rate on Na_2WO_4 concentration in the solution containing (mol l^{-1}): $CoSO_4$ – 0.1, NH_2CH_2COOH – 0.6, NaH_2PO_2 – 0.5 (1); with succinic acid 0.3 (2); pH 10.

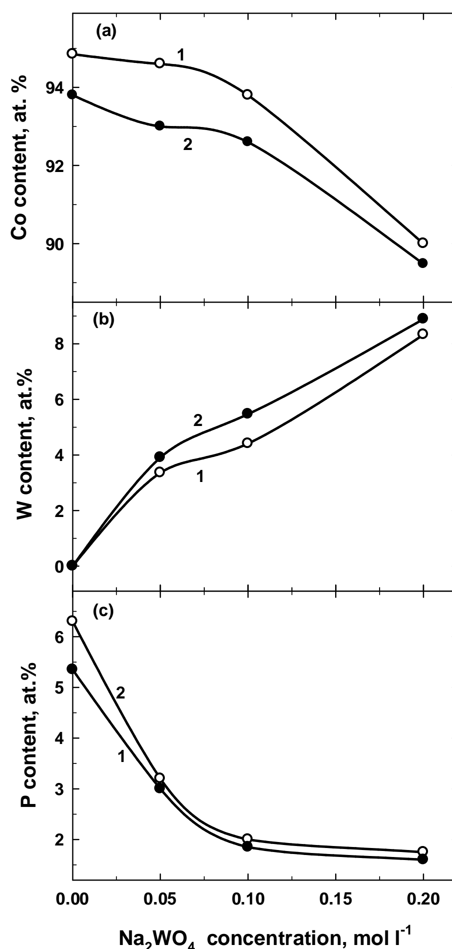
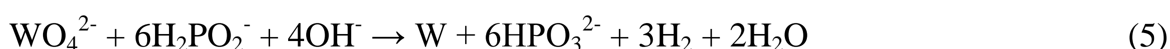


Fig. 3. Dependence of composition of the CoWP films on Na_2WO_4 concentration in the solution containing (mol l^{-1}): $CoSO_4$ – 0.1, NH_2CH_2COOH – 0.6, NaH_2PO_2 – 0.5 (1); with succinic acid – 0.3 (2); pH 10.

inverse ratio. An increase in concentration of sodium tungstenate diminishes the deposition rate (Fig. 2).

A tungsten incorporation into the CoP deposits results in the decrease in Co and P contents (Fig 3). It is evident that the reduction of tungsten(VI)-ions competes with Co and P ions reduction, which are related to some degree. The results obtained can testify that tungsten does not catalyze the reaction of sodium hypophosphite oxidation, which is the driving force in the overall electroless plating process. The mechanism of tungsten incorporation into CoP is not sufficiently clear yet, however the total reaction of the reduction of W(VI) may be written down:



$$WO_4^{2-} + 6H_2PO_2^- + 4OH^- \rightarrow W + 6HPO_3^{2-} + 3H_2 + 2H_2O \quad (5)$$

The difference between the microstructures of the CoP and CoWP films, deposited in a solution containing succinic acid on Cu, are distinctly seen in Fig. 4. The traces of the twined lamellas are seen along the longer axis almost in all CoP crystallites. R_{RMS} in a 0.2 µm CoP film is about 8.3 nm, while that in 1 µm - 13.4 nm. The grains of a CoWP film are distinguished by nearly equal axes. These films are rougher as compared with the CoP films; their R_{RMS} is about 9.5 nm in 0.2 µm films and 25 nm in the films of 1 µm thickness.

XRD patterns for the CoP and CoWP coatings were measured in the θ:θ mode and in a grazing incidence. According to the XRD patterns of the CoWP films measured in the grazing incidence mode, it has been determined that peaks position did not change significantly after heat-treatment (not shown). It could mean that Cu atoms did not diffuse into the upper layers of CoWP.

Figure 5 shows the XPS depth profiles of the CoP and CoWP films (about 0.4 µm in thickness) deposited on the Cu/Ta/SiO_2/Si substrate before and after heat-treatment at a temperature of 350 ^{o}C. After annealing of the CoP film at 350 ^{o}C for 30 min, the depth profile shows an appreciable diffusion of Cu atoms to cobalt or Co to Cu (Fig. 5 a, b). An alteration of diffusion layer reaches about 50 nm. Thus, the CoP thin layer is unsuitable to prevent Cu diffusion. While, after heat treatment of the CoWP film, any significant diffusion of Cu atoms into cobalt was not observed (Fig. 5 c, d). This fact confirms that the CoWP thin layer, deposited from a glycine-containing solution, serves as a perfect diffusion barrier to prevent Cu diffusion.

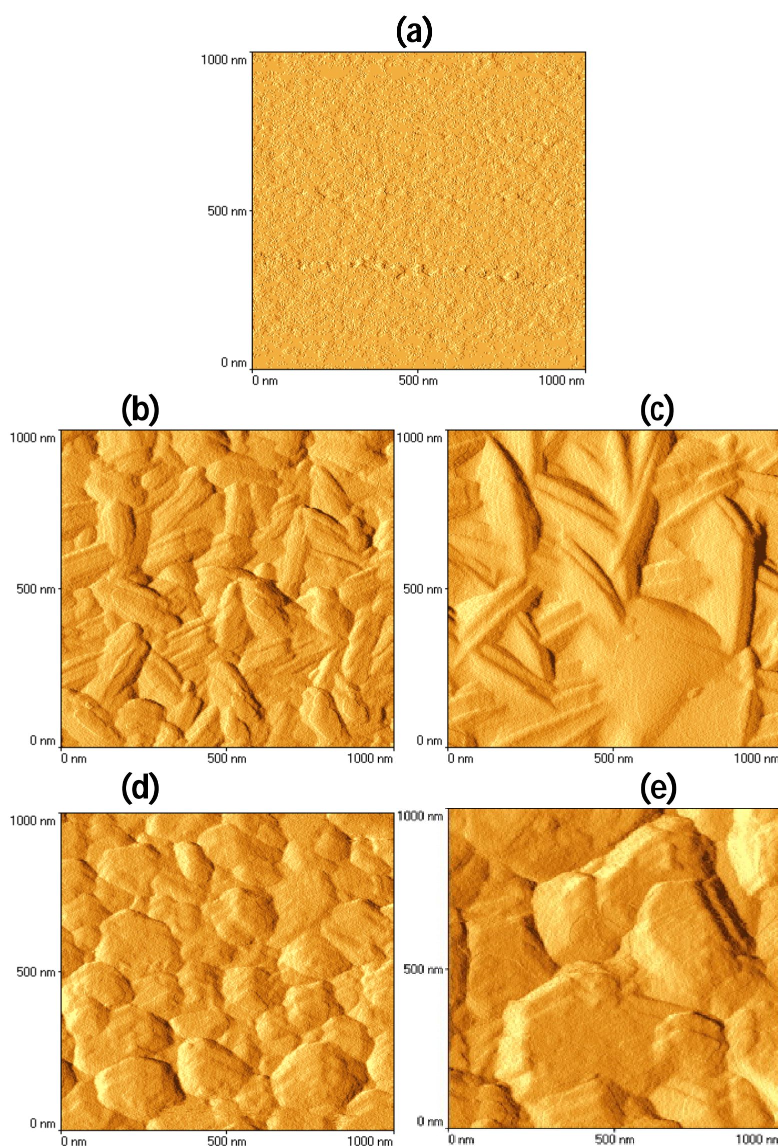
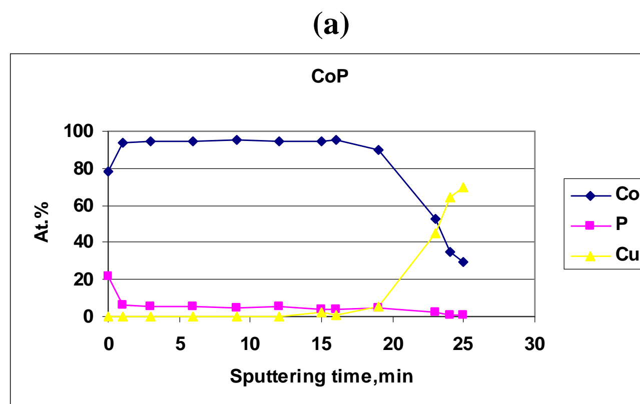
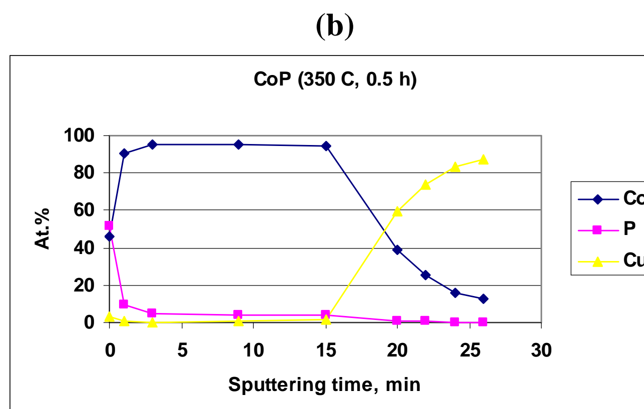


Fig. 4. AFM images of the Cu/Si substrate (a), CoP (b, c) and CoWP (d, e) films deposited on Cu/Si. CoP was deposited in the solution containing (mol l^{-1}): $CoSO_4$ - 0.1, NH_2CH_2COOH - 0.6, NaH_2PO_2 - 0.5, succinic acid - 0.3; pH 10. CoWP was deposited in the same solution containing 0.05 mol l^{-1} Na_2WO_4. Thickness of the films: b and d - 0.2 μm, c and e - 1 μm.

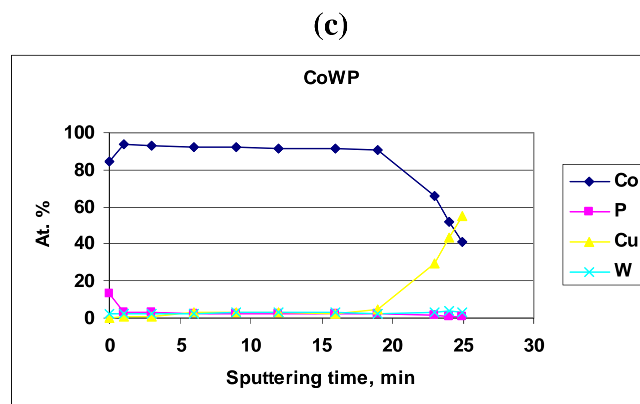
(a)



(b)



(c)



(d)

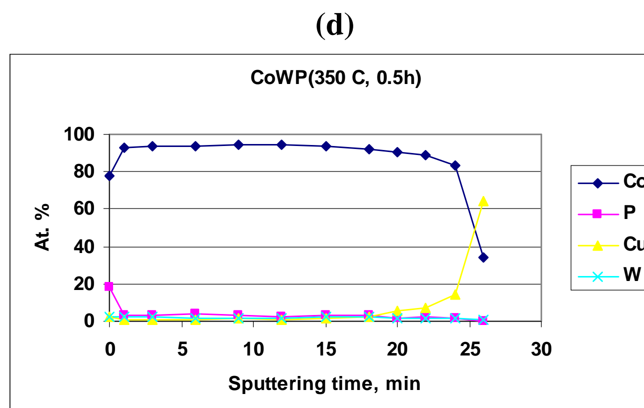


Fig. 5. XPS depth profiles of the CoP (a, b) and CoWP (c, d) films deposited in the solution containing (mol l^{-1}): $CoSO_4$ – 0.1, NH_2CH_2COOH – 0.6, NaH_2PO_2 – 0.5, succinic acid – 0.3 (a, b) and with Na_2WO_4 – 0.05 mol l^{-1} (c, d); pH 10; (a, c) initial, (b, d) after heat-treatment at 350 ^{o}C.

3.2. Cobalt films deposited using morpholine borane

If it is assumed that the reduction of cobalt using morpholine borane (MB) as a reducing agent proceeds in a similar manner to that was proposed for the reduction of Co(II) with DMAB, therefore it might be expressed by similar reactions. The initial stage of cobalt deposition an anodic oxidation of MB on the catalytic surface can be presented as follows:

$$C_4H_8ONH{\cdot}BH_3 + 3HOH + OH^- \rightarrow C_4H_8OH_2N^+ + B(OH)_4^- + 5H^+ + 6e \qquad (6)$$

The electrons produced from this reaction are used in cathodic reactions for the reduction of cobalt ions and boron:

$$C_4H_8ONH{\cdot}BH_3 + 4HOH + Co^{2+} \rightarrow Co + C_4H_8OH_2N^+ + B(OH)_4^- + 2H_2 + 2H^+ \qquad (7)$$

$$2C_4H_8ONH{\cdot}BH_3 + 2H^+ \rightarrow 2BH_3 + 2C_4H_8OH_2N^+ \rightarrow 2B + 2C_4H_8OH_2N^+ + 3H_2 \qquad (8)$$

At the same time some quantity of morpholine borane may be additionally consumed in the following unproductive catalytic decomposition reaction:

$$C_4H_8ONH{\cdot}BH_3 + 4H_2O \rightarrow C_4H_8OH_2N^+ + B(OH)_4^- + 3H_2 \qquad (9)$$

The rate of the cobalt film deposition grows markedly with increase in solution pH from 6 up to 8. This is explained by the acceleration action of OH^- ions to the first step of the process – to the rise of morpholine borane anodic oxidation rate (Eq. 6). The composition of the films obtained changes with solution pH. A slightly acidic medium is favorable for boron incorporation into the cobalt coatings. At pH 6.5 ca. 2 at. % of B was found in the cobalt films, at pH 7–7.5 only 0.5 at. % of B. It is evident that the reduction of cobalt (Eq. 7) is competitive with boron reduction (Eq. 8) and boron is incorporated into films. In spite of the fact that film analysis was performed at a depth of 40 nm, oxygen was also detected in films in all cases.

With increase in morpholine borane concentration in the solution anodic oxidation of MB accelerates, therefore, deposition rate increases markedly, particularly with increase in MB concentrations up to 0.05 mol l^{-1} (Fig. 7). The rise in the cobalt deposition rate with increase in concentration of MB in the solution is also connected with the changes in the composition of the films obtained. At pH 7.5 the quantity of cobalt in films decreases from 93.1 to 87.6 at. % with increase in MB concentration from 0.025 to 0.1 mol l^{-1}, whilst the boron quantity increases from 0.9 to 1.6 at. % and that of oxygen from 6 to 10 at. %.

A rise in Co(II) concentration up to 0.1 mol l^{-1} in a solution, containing 0.1 mol l^{-1} glycine and 0.05 mol l^{-1} MB, leads to a sharp increase in the cobalt deposition rate, whereas a subsequent increase in Co(II) concentration above 0.1 mol l^{-1}, slows down somewhat the films' deposition rate. This decrease is probably related to the lack of glycine for the active Co(II)-Gly complex.

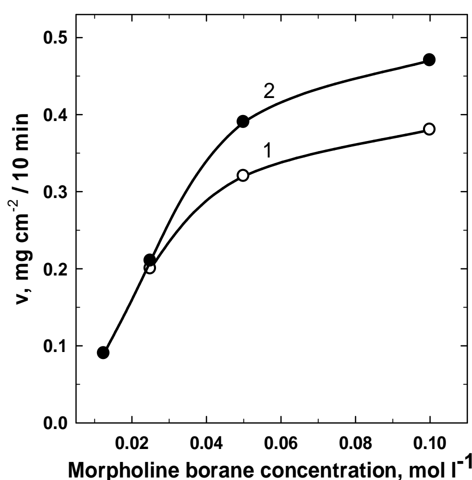


Fig. 7. Dependence of cobalt deposition rate on MB concentration in the solution containing (mol l^{-1}): $CoSO_4$ – 0.05; NH_2CH_2COOH – 0.1; pH 7 (1) and 7.5 (2).

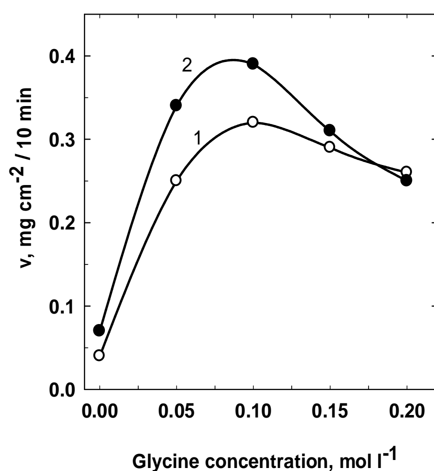


Fig. 8. Dependence of the Co films deposition rate on glycine concentration in the solution containing (mol l^{-1}): $CoSO_4$ – 0.05; MB – 0.05; pH 7 (1) and 7.5 (2).

The reduction of cobalt from the solution containing only Co(II) ions and a reducing agent may be performed, however it is very slow and the solution is unstable. With the addition of glycine both the stability of the solution and the rate of film deposition increase. A precisely specified concentration of glycine in the deposition solution is necessary for the given cobalt ions concentration to form the complex. The

highest deposition rate is reached at 0.1 mol l^{-1} glycine in solution when 0.05 mol l^{-1} of Co(II) is used, independent of pH in the chosen range, close to neutral (Fig. 8). A subsequent increase in glycine concentration leads to some decrease in film deposition rate. It is evident, the most active complex for cobalt discharge in close to neutral solutions is formed with a ratio of Co(II):Gly 1:2. Composition of the Co films dependently on glycinate concentration is presented in Fig. 9.

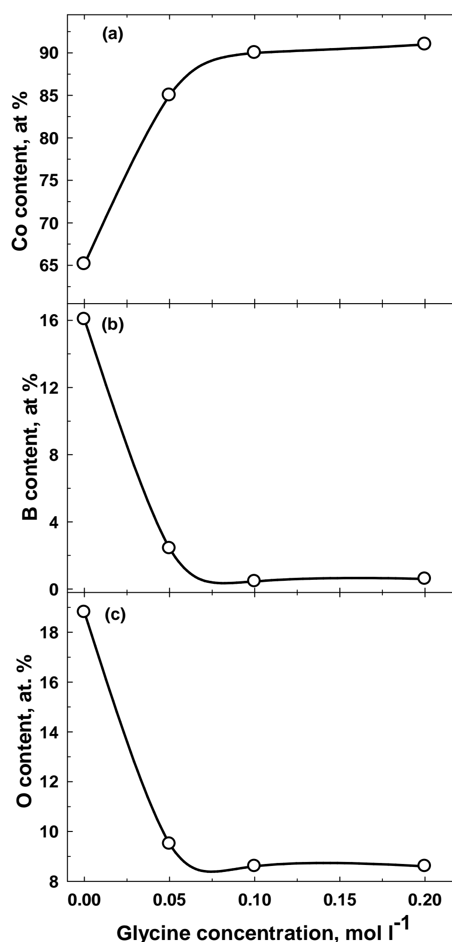


Fig. 9. Dependence of composition of the Co films on glycine concentration in the deposition solution containing (mol l^{-1}): $CoSO_4$ – 0.05; MB – 0.05; pH 7.

Both the boron and oxygen contents in the cobalt films are coherent; they both decrease with decrease in pH and glycine concentration, and increase with increase in MB concentration. From XPS spectra (Fig. 10) two boron species with different binding energies (E_b) were detected for the films containing a diminished cobalt quantity and enlarged boron and oxygen contents: elemental boron corresponding to the binding energy 187.7 eV and an oxygen-containing boron compound with a binding energy of 193.0 eV (which may conform to B_2O_3, H_3BO_3 or a similar compound). A certain

amount of oxygen was determined in all the cobalt films deposited using MB, similar to DMAB, despite the fact that films analysis was performed at a depth of 20–40 nm, even in the cases when the quantity of boron in the films was insignificant. According to the theoretical investigations, the catalytic oxidation of DMAB is a complex stepwise process, which eventually forms the boron oxygen containing compound $B(OH)_4^-$ via five-coordinate intermediates, in which OH^- coordinates to B before the elimination of the H radical. The reaction preferably proceeds at the solid/liquid interface. Such a mechanism for the reaction path may be proposed for electroless deposition using morpholine borane. Boron-oxygen containing compounds may be involved in the cobalt coating. This may explain why oxygen always is determined together with boron in the cobalt films. The distribution between elemental boron and boron oxygen-containing compound found in the cobalt film is dependent on glycine concentration in the deposition solution as shown in Table 2.

Table 2. Boron species (agreeably to XPS analysis) incorporated into the Co films dependently on glycine concentration in the deposition solution containing (mol l^{-1}): $CoSO_4$ – 0.05, MB – 0.05, NH_2CH_2COOH – 0 - 0.2; pH 7.0. Data of XPS analysis are given for films at a depth of 40 nm.

Glycine, mol l^{-1}	B (E_b = 187.7 eV), at. %		B ox. (E_b = 193.0 eV), at. %	
	in CoB 0.1 μm	in CoB 1 μm	in CoB 0.1 μm	in CoB 1 μm
–	10.4	13.1	5.2	6.53
0.1	1.34	1.39	1.94	2.26
0.2	–	–	0.54	0.86

The highest quantities of both elemental boron and its oxygen-containing compound were found when deposition was performed without a complexing agent and when the reduction of cobalt is very slow, therefore boron reduction may proceed without evident competition. With increase in glycine concentration in solution, corresponding to active Co-Gly complex formation, boron reduction is hindered owing to the acceleration of Co reduction, therefore, elemental boron in the film gradually vanishes. The decrease in the quantity of oxygen-containing boron compounds in films is determined by the increased Co reduction rate (Eq. 7) and improved stability of deposition solution that is why the catalytic oxidation of MB (Eq. 9) proceeds to a lesser

degree. Thus, the cobalt films deposited in fairly complexed solutions have only a marginal quantity of boron or sometimes not even detected. The data presented in Table 2 show that contents of both types of boron slightly increase with increase in thickness of films.

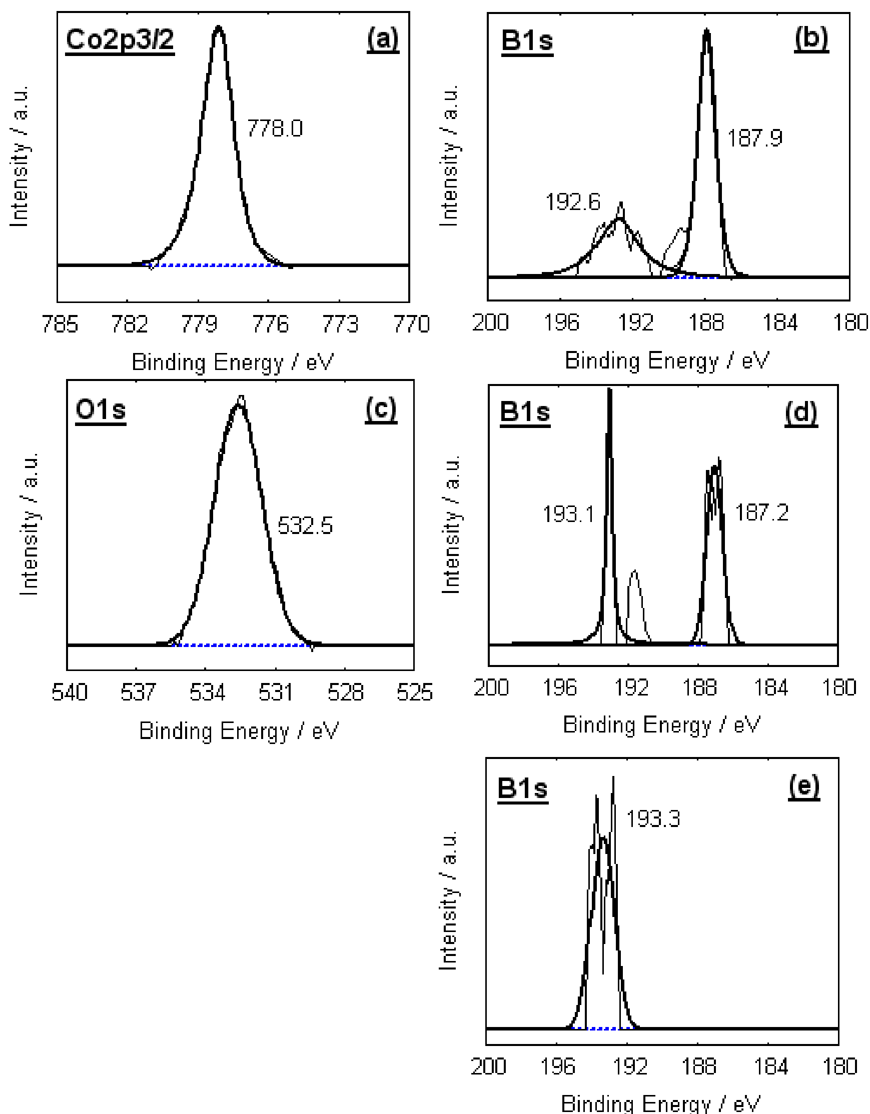


Fig. 10. XPS spectra of $Co2p_{3/2}$ (a), O1s (c) and B1s (b, d, e) of films deposited in the solutions containing (mol l^{-1}): $CoSO_4$ – 0.05, MB – 0.05, Glycine – 0-0.2; pH 7.0. B1s spectra are obtained for the Co films deposited without glycine (b) and with glycine (mol l^{-1}): 0.1 (d), 0.2 (e). XPS spectra are given for films at a depth of 40 nm.

3.3 The Au/Co/Cu and Au/CoB/Cu catalysts and studies of their catalytic properties towards borohydride oxidation

The Au/Co/Cu and Au/CoB/Cu catalysts were prepared by a two-step process which involves electroless cobalt deposition followed by a spontaneous gold displacement from the acidic $HAuCl_4$ and neutral $KAu(CN)_2$ solutions with the aim to

use them as electrocatalysts in direct borohydride fuel cells. The electroless Co or CoB layers were used as an underlayer for the formation of immersion gold overlayer onto the copper surface. When electroless cobalt plating was performed without glycine, the obtained Co coatings contained ca. 10.4-13.0 at. % of B (Table 2), whereas in the presence of 0.2 mol l^{-1} glycine practically pure Co coatings were obtained. The thickness of the pure Co and Co containing boron coatings was ca. 0.9 μm. The Co or CoB coatings deposited on the copper surface have a fine structure consisting of small Co crystallites in sizes 6 to 25 nm.

The Au/Co/Cu and Au/CoB/Cu catalysts were obtained by immersion of Co/Cu or CoB/Cu into the acidic $HAuCl_4$ solution at 25 °C and neutral $KAu(CN)_2$ solution at 30 ° for 0.5, 1 and 5 min, respectively. Immersion of Co/Cu or CoB/Cu into the both gold-containing solutions for 0.5, 1 and 5 min, respectively, results in the formation of Au nanoparticles of the cubic shape on the Co/Cu and CoB/Cu surfaces. The Au nanoparticles were homogeneously dispersed on the copper surface. The size of deposited Au crystallites on the Co/Cu or CoB/Cu electrodes depends on the composition of gold-containing solutions. After immersion of Co/Cu and CoB/Cu into the acidic $HAuCl_4$ solution at 25 °C and neutral $KAu(CN)_2$ solution at 30 °C for 0.5, 1 and 5 min, the Au crystallites of 6-50 and 4-12 nm in size, respectively, were deposited on the copper surfaces. It has been determined that the Au loadings were 9.3, 11.6 and 36.1 μg cm^{-2} in the as-prepared Au/Co/Cu catalysts after immersion of the Co/Cu electrodes into the acidic $HAuCl_4$ solution at 25 °C for 0.5, 1 and 5 min, respectively. The Au loadings were 8.0, 14.3 and 44.2 μg cm^{-2} in the as-prepared Au/CoB/Cu catalysts after immersion of the CoB/Cu electrodes into the acidic $HAuCl_4$ solution at 25 °C for 0.5, 1 and 5 min, respectively. The Au loadings were 5.8, 7.1 and 15.3 μg cm^{-2} in the as-prepared Au/Co/Cu catalysts after immersion of the Co/Cu electrodes into the neutral $KAu(CN)_2$ solution at 30 °C for 0.5, 1 and 5 min, respectively. The Au loadings were 3.1, 5.2 and 14.0 μg cm^{-2} in the as-prepared Au/CoB/Cu catalysts after immersion of the CoB/Cu electrodes into the neutral $KAu(CN)_2$ solution at 30 °C for 0.5, 1 and 5 min, respectively.

According to the data of XRD analysis of the Au/Co/Cu catalysts containing approximately the same amount of Au (according to EDX data) but the Au crystallites

were deposited on the Co/Cu surfaces using different gold-containing solutions: acidic $HAuCl_4$ and neutral $KAu(CN)_2$, it has been determined that Au particles is composed of larger crystallites and the growth process was faster from the acidic $HAuCl_4$ solution since the same load of Au was achieved during 1 minute while in neutral $KAu(CN)_2$ solution the deposition took 5 minutes.

The oxidation of BH_4^- ions on differently formed catalysts was investigated by cyclic voltammetry. Figure 11 presents the comparison of the stabilized positive-potential going scans (5th cycles) of the oxidation of BH_4^- ions recorded on the bare Au (*dotted line*), Co/Cu (a, b, *solid line*), CoB/Cu (c, d, *solid line*), Au/Co/Cu (a, b), and Au/CoB/Cu (c, d) catalysts with different Au loadings in a 0.05 mol l^{-1} $NaBH_4$ + 1 mol l^{-1} NaOH solution at a potential scan rate of 10 mV s^{-1}.

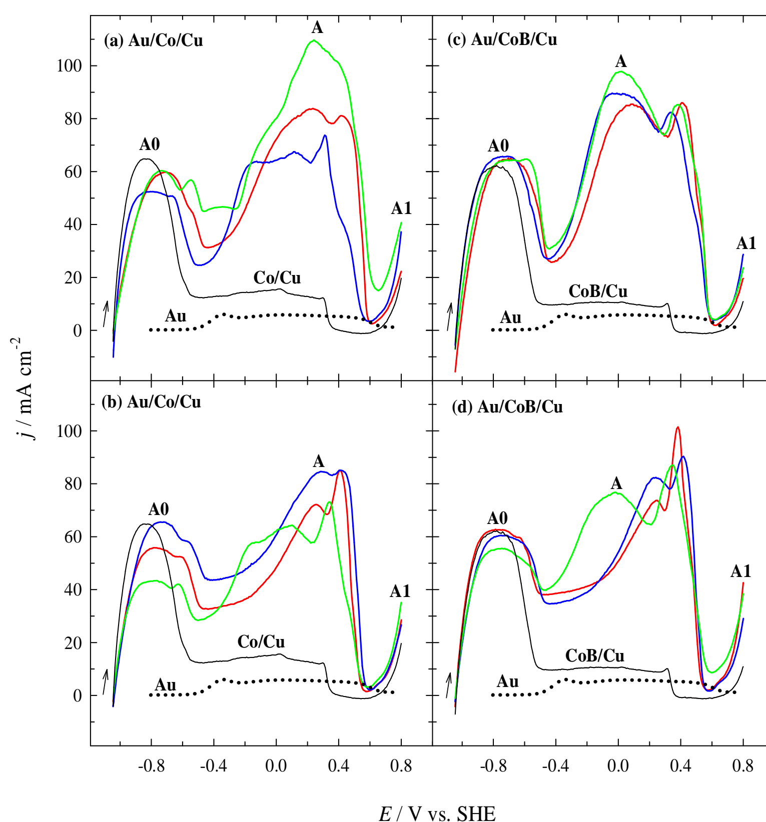


Fig. 11. Stabilized positive-potential going scans (5th) of the Au (*dotted line*), Co/Cu (a, b, *solid lines*), CoB/Cu (c, d, *solid lines*), Au/Co/Cu (a, b) and Au/CoB/Cu (c, d) catalysts recorded in 0.05 M $NaBH_4$ + 1 M NaOH at a potential scan rate of 10 mV s^{-1} at 25°C. The Au/Co/Cu (a, b) and Au/CoB/Cu (c, d) catalysts were prepared by immersion of the Co/Cu and CoB/Cu catalysts into 1 mM $HAuCl_4$ (pH 1.8) at 25 °C (a, c) and 5 mmol l^{-1} $KAu(CN)_2$ + 0.4 mol l^{-1} $(NH_4)_2C_6H_6O_7$ complex (pH 5.0) at 30 °C (b, d) for 0.5 min (*red line*), 1 min (*blue line*) and 5 min (*green line*).

Two well-expressed anodic peaks **A0** at lower potential values and peak **A** at more positive potential values are recorded in the CVs for the Au/Co/Cu and Au/CoB/Cu (Fig. 11). Anodic peak **A0** is attributed to the oxidation of H_2 generated by catalytic hydrolysis of BH_4^-, whereas anodic peak **A** is related with direct borohydride oxidation as described in literature. As seen from the data in Fig. 11, current densities of anodic peak **A0** recorded on the obtained Au/Co/Cu and Au/CoB/Cu catalysts with different Au loadings have rather similar values as on the bare Co/Cu or CoB/Cu catalysts. The peak **A** current density values are significantly higher on the different Au/Co/Cu and Au/CoB/Cu catalysts as compared to bare Au or Co/Cu and CoB/Cu. In the case of the Au/Co/Cu and Au/CoB/Cu catalysts prepared by immersion of the Co/Cu or CoB/Cu catalysts into the acidic $HAuCl_4$ solution for 0.5, 1 and 5 min, respectively, the obtained current densities of anodic peak **A** are ca. 14-12-19 times higher at Au/Co/Cu with the Au loadings of 9.3, 11.6 and 36.1 μg cm^{-2}, respectively, and ca. 15-16-17 times higher at Au/CoB/Cu with the Au loadings of 8.0, 14.3 and 44.2 μg cm^{-2}, respectively, as compared with those at bare Au (Fig.11 a, c). Current densities of peak **A** are also 5.3-4.3-7.0 and 8.0-8.4-9.1 times higher at the above mentioned Au/Co/Cu and Au/CoB/Cu catalysts with different Au loadings as compared to those at the Co/Cu or CoB/Cu catalysts (Fig. 11 a, c).

Similar data were obtained for the Au/Co/Cu and Au/CoB/Cu catalysts prepared by immersion of Co/Cu or CoB/Cu catalysts into the neutral $KAu(CN)_2$ solution for 0.5, 1 and 5 min, respectively (Fig. 9b, d). Peak **A** current density values recorded on the Au/Co/Cu catalysts with the Au loadings of 5.8, 7.1 and 15.3 μg cm^{-2} and Au/CoB/Cu catalysts with the Au loadings of 3.1, 5.2 and 14.0 μg cm^{-2} are ca. 12-15-11 and 13-14-13, respectively, times greater as compared to those on bare Au (Fig. 9b, d). Current densities of anodic peak **A** are ca. 4.8-5.4-4.1 times higher at the Au/Co/Cu catalysts with the Au loadings of 5.8, 7.1 and 15.3 μg cm^{-2} and Au/CoB/Cu catalysts with the Au loadings of 3.1, 5.2 and 14.0 μg cm^{-2}, respectively, as compared with those at the Co/Cu and CoB/Cu catalysts (Fig. 11 c, d). An enhanced electrocatalytic activity of the investigated Au/Co/Cu and Au/CoB/Cu catalysts with low Au loadings under peak **A** related with the direct oxidation of BH_4^- ions may be attributed to the intrinsic electrocatalytic activity of the Au nanoparticles deposited on the Co/Cu and CoB/Cu surfaces.

To compare the catalytic activity of the investigated Au/Co/Cu and Au/CoB/Cu catalysts, the current density values were normalized in reference to the Au loadings for each catalyst (Fig. 12). As seen from the data in Fig. 12, the highest mass activity (A mg_{Au}^{-1}) for the both oxidation peaks **A0** at -0.9 V and **A** at 0 V has the Au/CoB/Cu catalyst with the Au loading of 3.1 μg cm^{-2} and with deposited Au nanoparticles in size of ca. 4 nm (Fig. 12b,d), prepared from a neutral $KAu(CN)_2$ solution (Fig. 12d).

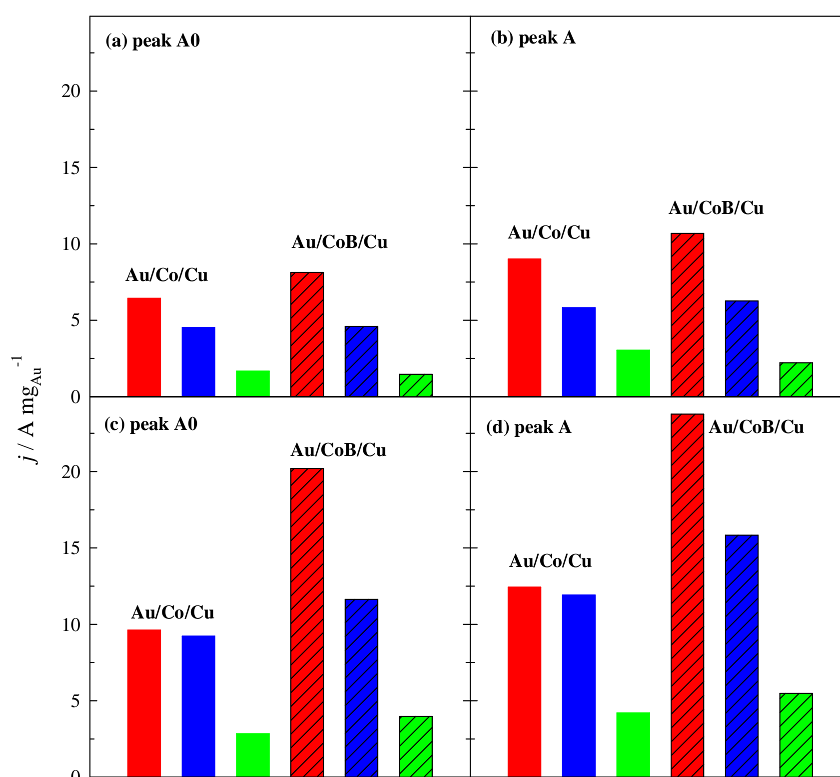


Fig. 12. Bar plots of Au-metal mass activity for borohydride oxidation obtained from Au/Co/Cu and Au/CoB/Cu catalysts at a potential of peak **A0** (a,c) and **A** (b,d) derived from Fig. 11. The Au/Co/Cu and Au/CoB/Cu catalysts were prepared by immersion of the Co/Cu and CoB/Cu catalysts into 1 mmol l^{-1} $HAuCl_4$ (pH 1.8) at 25 ^{o}C (a, b) and 5 mmol l^{-1} $KAu(CN)_2$ + 0.4 mol l^{-1} $(NH_4)_2C_6H_6O_7$ complex (pH 5.0) at 30 ^{o}C (c, d) for 0.5 min (*red*), 1 min (*blue*) and 5 min (*green*).

The electrochemical behavior of the Au/Co/Cu and Au/CoB/Cu catalysts with low Au loadings as compared to that of Au and Co/Cu or CoB/Cu for both processes: the oxidation of H_2 generated by catalytic hydrolysis of BH_4^- (peak **A0**) at -0.9 V and direct borohydride oxidation (peak **A**) at 0 V was investigated under chronoamperometric conditions (not shown). The chronoamperometry studies also confirmed high Au/Co/Cu

and Au/CoB/Cu catalytic activities for the oxidation of BH_4^- ions as compared to that of Au, Co/Cu and CoB/Cu.

A series of the Au/Co/Cu and Au/CoB/Cu catalysts with low Au loadings were prepared by a simple way which involves electroless Co deposition followed by a spontaneous Au displacement from the different gold-containing solutions. The prepared Au/Co/Cu and Au/CoB/Cu catalysts with the Au loadings in the range from 3 to 44 µg Au cm^{-2} and with deposited Au nanoparticles in size of ca. 4-50 nm demonstrated a significantly higher electrocatalytic activity towards the oxidation of BH_4^- ions as compared to those of bare Au or Co/Cu and CoB/Cu.

The prepared Au/Co/Cu and Au/CoB/Cu catalysts with low Au loadings seem to be promising for direct borohydride fuel cells.

4. CONCLUSIONS

While electrolessly depositing Co coatings in the glycine-containing solutions using sodium hypophosphite as a reducing agent:

1. It has been determined that using sodium hypophosphite as a reducing agent the rate of CoP and CoWP coatings deposition and the quantity of P in the coatings rise with increase in solution pH; the increase in tungstate concentration results decrease in plating rate and quantity of P in the coatings. After appropriate conditions were selected, high-quality cobalt coatings containing from 2.9 to 6.3 at. % of P and up to 5 at. % of W were obtained.
2. It has been found that fatty dicarbonic acids improve the buffering properties of the solutions, accelerate the deposition rate of the cobalt coatings and increase the quantity of phosphorus in them. The buffering properties of the solutions improve with an increase in the number of $-CH_2-$ groups in the chain of dicarbonic acid.
3. The XRD and XPS data obtained suggest that thin CoWP coatings deposited in the glycine-containing solution are an appropriate barrier against Cu migration into adjacent layers.

While electrolessly depositing Co coatings in the glycine-containing solutions using morpholine borane as a reducing agent:

4. It has been found that both nearly pure cobalt coatings free from boron and coatings containing up to 13 at. % of boron can be obtained at a relatively low temperature of 30 ^{o}C.
5. It has been determined that boron in cobalt coatings can exist in two forms: elemental boron (E_b = 187.7 eV) and boron in form of its oxycompounds (E_b = 193.0 eV).
6. It has been shown that increase in glycine concentration in electroless cobalt plating solutions diminishes nonproductive consumption of morpholine borane.
7. It has been found that the nanostructured Au/Co/Cu and Au/CoB/Cu catalysts with the Au loadings in the range from 3 to 44 μg Au cm^{-2} and with deposited Au nanoparticles in size of ca. 4-50 nm demonstrated a higher electrocatalytic activity towards the oxidation of BH_4^- ions, as compared to those of bare Au or Co/Cu and CoB/Cu and seem to be promising for direct borohydride fuel cells.

8. It has been shown that the highest mass activity towards the electro-oxidation of borohydride exhibits the Au/CoB/Cu catalyst with the Au loading of 3.1 μg Au cm^{-2} and with deposited Au nanoparticles in size of ca. 4 nm.

List of Publications

1. R. Tarozaitė, **Z. Sukackienė**, A. Sudavičius, R. Juškėnas, A, Selskis, A. Jagminienė, E. Norkus. *"Application of glycine containinig soliutions for electroless deposition of Co-P and Co-W-P films and their behavior as barrier layers"*. Materials Chemistry and Physics **117**, N 1 (2009) 117-124.
2. R. Tarozaitė, A. Sudavičius, **Z. Sukackienė**, E. Norkus. *"Electroless cobalt deposition in the glycinate soliution using morpholine borane as a reducing agent"*. Transactions of the Institute of Materials Finishing **92**, N 3 (2014) 146-152.

Other Publications

1. **Z. Sukackienė**, A. Balčiūnaitė, A. Selskis, L. Tamašauskaitė - Tamašiūnaitė, E. Norkus. *"Investigation of borohydride oxidation on nanostructured Au/Co surface"*. Chemistry and Chemical Technology of Inorganic Materials, Kaunas (2013) 26.
2. **Z. Sukackienė**, A. Balčiūnaitė, L. Tamašauskaitė-Tamašiūnaitė, V. Pakštas, A. Selskis, E. Norkus *"Development of new nanostructured Au/Co/Cu and Au/CoB/Cu catalysts and studies of their catalytic activity*". ECS Transaction from the ECSEE "Electrochemical Conference of energy & the Environment". Shanghai, China (2014) (in print).

Conferences Materials

Oral presentations:

1. **Z. Sukackienė**, A. Balčiūnaitė, L. Tamašauskaitė-Tamašiūnaitė, V. Pakštas, A. Selskis, E. Norkus. *„Development of new nanostructured Au/Co/Cu and Au/CoB/Cu catalysts and studies of their catalytic activity*" (2014) "Electrochemical Conference of energy & the Environment". Shanghai, China (2014) 31.
2. **Zita Sukackienė**. *„Cheminis kobalto dangų nusodinimas glicininiuose tirpaluose naudojant reduktoriumi morfolino boraną*". LMA III jaunųjų mokslininkų konferencija "Fizinių ir technologijos mokslų tarpdalykiniai tyrimai". Vilnius (2013) 16.

3. **Zita Sukackienė**. „*Co-P ir Co-P-W lydinių nusodinimas siekiant sukurti variui barjerinį sluoksnį“.* 1 - oji FTMC doktorantų ir jaunųjų mokslininkų konferencijos pranešimų medžiaga. Vilnius (2010) 9.

Poster presentations:

4. **Z. Sukackienė**, R. Tarozaitė “*Studies of morpholine borane catalytic consumption in electroless cobalt plating soliutions”*. 11th International Conference of Lithuania's Chemists. Vilnius (2013) P50.

5. **Z. Sukackienė**, A. Balčiūnaitė, A.Selskis, L. Tamašauskaitė-Tamašiūnaitė, E. Norkus *“Formation of effective nanostructured Au/CoB/Cu catalysts and studies of their catalytic properties towards borohydride oxidation”*. 15-th International Conference-School Advanced Materials and technologies. Palanga (2013) 56.

6. **Z. Sukackienė**, A. Balčiūnaitė, A. Selskis, L. Tamašauskaitė – Tamašiūnaitė, E. Norkus. „*Investigation of borohydride oxidation on nanostructured Au/Co surface”*. Respublikinė konferencija “Neorganinių medžiagų chemija ir technologija”. Kaunas (2013) 26.

7. R. Tarozaitė, **Z. Sukackienė,** A. Sudavičius. „*Electroless deposition of Co-P and Co-W-P films from glycine containing solutions as barrier layers against Cu diffusion*“.9-th conference of Lithuanian chemists „Chemistry 2009” dedicated for 110th anniversary of academician Juozas Matulis. Vilnius (2009) 83.

8. **Z. Jasinskaitė (Sukackienė),** R. Tarozaitė, A. Sudavičius, E. Norkus. „*Electroless deposition of CoP and CoPW coatings in glycinate soliutions*“.8th conference of Lithuanian chemists „Chemistry 2007” dedicated for 210 anniversary of Faculty of Chemistry of Vilnius University. Vilnius (2007) 52.

KOBALTO IR JO LYDINIŲ CHEMINIO NUSODINIMO YPATUMŲ TYRIMAS

Santrauka

Iškilus naujiems technologiniams uždaviniams, cheminės dangos kobalto pagrindu pradėtos naudoti mikroelektronikoje ir mikromechanikoje, siekiant sudaryti apsauginį sluoksnį vario migracijai integralinėse schemose. Varis turi mažą specifinę varžą, tačiau turi ir keletą trūkumų, tokių kaip blogas korozinis atsparumas ir aukštas difuzijos koeficientas į Si ir SiO_2 bei kitas medžiagas. Šios problemos gali būti sumažintos naudojant ploną barjerinį sluoksnį, apsaugantį nuo vario difuzijos. Tam tinka CoP bei CoB sluoksnių barjerinės savybės, kurias galima pagerinti įvedant volframą.

Taip pat pastaruoju metu skiriamas didelis dėmesys naujų medžiagų paieškai, kurias galima būtų taikyti tiesioginiuose borhidrido kuro elementuose kaip anodo medžiagas.

Mūsų darbo tikslas - ištirti kobalto dangų cheminio nusodinimo glicininiuose tirpaluose ypatumus, reduktoriais naudojant natrio hipofosfitą ir morfolino boraną, bei nustatyti gaunamų dangų sudėtį ir jų panaudojimo galimybes barjerinių sluoksnių formavimui ant vario bei taikymui kuro elementų gamybai.

Nustatyta, kad dikarboninės rūgštys gerina tirpalų buferines savybes, pagreitina kobalto dangų nusėdimą ir didina fosforo kiekį jose. Tirpalų buferinės savybės gerėja, augant -CH_2- grupių skaičiui dikarboninės rūgšties grandinėje. Nustatyta, kad, didinant tirpalų volframato jonų koncentraciją kobalto dangų nusėdimo greitis ir P kiekis jose mažėja. Parinkus tinkamas sąlygas buvo gautos kokybiškos kobalto dangos, į kurias patenka nuo 2,9 iki 6,3 at.% P ir nuo 3 iki 5 at. % W. XRD ir XPS tyrimais nustatyta, kad plonos CoWP dangos, nusodintos glicininiame tirpale, yra tinkamas barjeras Cu migracijai į ribojančius sluoksnius.

Nusodinant chemines kobalto dangas, reduktoriumi naudojant morfolino boraną ir esant santykinai žemai kobaltavimo tirpalo temperatūrai 30 °C, buvo gautos praktiškai gryno kobalto dangos, savo sudėtyje neturinčios boro, bei dangos, į kurias patenka iki 13 at. % boro. Nustatyta, kad kobalto dangose gali būti dvi boro atmainos: elementinis boras (E_b = 187,7 eV) ir boras deguoniniuose junginiuose (E_b = 193,0 eV). Nusodinant

kobalto dangas, glicino koncentracijos didinimas kobaltavimo tirpaluose sumažina neproduktyvų morfolino borano sunaudojimą.

Nanostruktūrizuoti Au/Co/Cu ir Au/CoB/Cu katalizatoriai buvo suformuoti, taikant cheminį kobalto dangų nusodinimą bei imersinį jų padengimą auksu. Parodyta, kad Au/Co/Cu ir Au/CoB/Cu katalizatoriai su nusodinto Au įkrova nuo 3 iki 44 $\mu g\ cm^{-2}$ bei nusodinto Au nanadalelėmis ~4-50 nm dydžio pasižymi ženkliu elektrokataliziniu aktyvumu borhidrido oksidacijos reakcijai ir gali būti naudojami tiesioginiuose borhidrido kuro elementuose kaip anodo katalizatorius. Nustatyta, kad didžiausiu kataliziniu aktyvumu (A mg_{Au}^{-1}) borhidrido oksidacijos reakcijai pasižymi Au/CoB/Cu katalizatorius su nusodinto aukso įkrova 3,1 μg Au cm^{-2}, gautas imersiškai nusodinus ~4 nm dydžio Au daleles ant CoB paviršiaus, naudojant 5 mmol l^{-1} $KAu(CN)_2$ + 0.4 mol l^{-1} $(NH_4)_2C_6H_6O_7$ tirpalą (pH 5,0).

Information about the author

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2000-2004	Bachelor degree of Chemistry, Vilnius University, Faculty of Chemistry
2004-2006	Master degree of Chemistry and teacher qualification, Vilnius Pedagogical University
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