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Electrochemical codeposition of molybdenum and selenium

Elektrochemiczne osadzanie molibdenu z selenem

Abstract
The electrodeposition of Mo-Se thin films from a sulfate solution containing Na_2MoO_4 and H_2SeO_3 was studied. The process of deposition was conducted under potentiostatic conditions on a copper electrode. The effect of potential value, pH, and time of deposition were examined. The deposits were characterized by X-ray diffraction, X-ray fluorescence, and scanning electron microscopy. The obtained results have shown the possibility of co-deposition of molybdenum and selenium with different stoichiometric ratios.

Keywords: electrodeposition, molybdenum, selenium, transition metal chalcogenides

Streszczenie
Przeprowadzono badania dotyczące procesu elektrochemicznego osadzania molibdenu z selenem z roztworów siarczanowych zawierających Na_2Mo_4 i H_2SeO_3. Proces osadzania przeprowadzono w warunkach potencjostatycznych na elektrodach miedzianych. Zbadano wpływ potencjału, pH elektrolitu oraz długości czasu osadzania na jakość otrzymanych powłok. Otrzymane warstwy były badane z wykorzystaniem dyfrakcji rentgenowskiej, spektrofluorymetrii rentgenowskiej oraz skaningowego mikroskopu elektronowego. Wykazano możliwość otrzymania powłok o różnym stosunku molibdenu do selenu.

Słowa kluczowe: elektroosadzanie, molibden, selen, chalkogenki metali przejściowych

1. Introduction

Transition metal chalcogenides are a wide group of compounds that have band gaps from 0 to 2 eV with very promising optoelectronic properties, enabling the transition

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from an indirect-band gap in the thick n-monolayer film to a direct-band gap in the single layers. Among them, molybdenum chalcogenides (MoS_2, $MoSe_2$) have been investigated as electrocatalysts for hydrogen evolution as an alternative to very expensive platinum [1]. Their morphologies and properties are also useful for energy storage applications such as electrodes for Li-ion batteries, supercapacitors [2, 3], and solid lubricants [4]. In addition, the Mo_3Se_4 compound has a remarkable physical property; namely, it is a superconductor with an extremely high upper-critical magnetic field [5].

Usually transition metal chalcogenide compounds can be obtained in thin film form by various methods, including sputtering, chemical bath deposition, selenization, solid state reactions, sulphurization, and electrodeposition [6, 7]. The last one is commonly used as a beneficial technology in producing films and coatings of metals and alloys [8, 9], semiconductors [10–12], and (more specifically) materials used to produce photovoltaic cells [11] or catalysts applied in the hydrogen-production process [13, 14].

An analysis of the electrochemical process of the co-deposition of selenium with molybdenum is interesting in light of the possibilities of Se-Mo alloy deposition [15–20]. Taking into consideration the many existing methods used for obtaining alloy coatings, factors favoring the development of electrochemical methods are the low cost of conducting the process, the ability to coat surfaces of complex shapes, and the possibility for precise control of processes taking place during coatings deposition (i.e., their composition, morphology, structure, and thickness). On the other hand, the electrodeposited coatings are very often amorphous or fine-grained, which is a disadvantage due to the worsened electrical and optical properties. Therefore, the electrodeposited material layers need an additional post-deposition annealing step in a suitable atmosphere in order to improve crystallinity. One other disadvantage of electrodeposition is that it is only possible to apply conducting materials as a substrate.

The electrodeposition of thin films of Mo-Se phases from aqueous baths was studied. The effect of pH on the electrolyte and applied potential were examined. The applied pH and potential of electrolysis were changed systematically in ranges where it significantly effects on the composition of Mo-Se thin films. The composition and structure of the deposited thin films were identified by WD-XRF and XRD techniques. Moreover, the morphology of the samples was analyzed by SEM.

2. Experimental

A conventional three-electrode system was employed, with a platinum foil as a counter electrode (6 cm^2) and a saturated calomel electrode (SCE) as the reference electrode. The substrate for electrodeposition was a copper sheet (2.8 cm^2). The copper sheets were chemically etched in the HNO_3:CH_3COOH:H_3PO_3 1:1:1 mixture for 60 s at a temperature of 60°C before the process of deposition. All chemicals used in this work were of analytical grade. Concentrations of the solutions were 0.002 mM H_2SeO_3 and 0.05 M Na_2MoO_4. The pH of the electrolyte was changed in a range between 2 and 8. The pH was adjusted by the addition of sulfuric acid or sodium hydroxide. Additionally, sodium sulfate was added to the solution to increase conductivity. The EDAQ EA163 potentiostat was used for the deposition process in the potentiostatic mode. The film growth was carried out for a different time. XRD diffraction patterns were registered with a Rigaku Miniflex II diffractometer with Cu K_a radiation. The morphology of the coatings was studied with the use of scanning electron microscopy (SEM) on an SU 70 instrument (Hitachi). The chemical composition of electrodeposits was characterized by the wavelength-dispersive X-ray fluorescence method (WDXRF) by Rigaku PriMini.

3. Results and discussion

According to thermodynamic predictions, the process of metal chalcogenide synthesis can be achieved when a large excess of less-noble ions is present in the solution [21, 22]. It is the result of the electrochemical properties of selenium compared to the co-deposited metals in aqueous solutions and the free energy of formation of the compounds. According to the Mo-Se binary phase diagram [23], two binary compounds of $MoSe_2$ and Mo_3Se_4 are known to be thermodynamically stable. Proper adjustment of the bath composition should lead to the formation of stoichiometric compounds, and may exclude the presence of an excess of selenium while the solid phase is being formed [24–26]. Consequently, electrolysis was carried out in the solution containing 0.002 M H_2SeO_3 and 0.05 M Na_2MoO_4. Selenium and molybdenum have different ionic forms strongly dependant on the pH of the electrolyte. The chemistry of both elements in aqueous solutions are very well described in the literature [27–29].

Due to the preliminary character of our research, the mechanism for the reduction of selenium and molybdenum were simplified, and the basic forms were used. The process of electrodeposition starts with an initial formation of an Se layer according to the reaction:

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \tag{1}$$

The presence of H_2SeO_3 in the electrolyte bath shifts the cathodic current to the region of more positive potential and enables the deposition of molybdenum [29]. The theoretical redox reaction associated with the deposition of Mo can be represented by the reaction [27, 29, 30]:

$$H_2MoO_4 + 6H^+ + 6e^- \rightarrow Mo + 4H_2O \tag{2}$$

When molybdenum atoms are electrodeposited, the formation of chalcogenides could be possible:

$$xMo + ySe \rightarrow Mo_xSe_y \tag{3}$$

It is also important to point out that molybdenum oxide formation is possible according to thermodynamic predictions during electrodeposition [27]. But during the codeposition with other elements (e.g., with Ni), they have a tendency to behave as intermediate and are subsequently reduced to metallic form [31, 32]. It is expected that selenium can play the same role as nickel and "induce" the deposition of molybdenum from an aqueous solution and simultaneously create selenides.

A detailed study was carried out by changing the pH of the electrolyte by a wide range. The deposition time in each case was equal to 15 minutes. It was found that the chemical composition of the Mo-Se films strongly depends on the pH of the solution. Table 1 presents the Mo/Se ratio in the films.

Table 1. Composition of the deposited coatings from electrolyte 0.05 M Na_2MoO_4, 0.002 M H_2SeO_3, 0.1 M Na_2SO_4, T = 55°C at different pH

Deposition potential	**Mo/Se % at. ratio**					
	pH = 3	**pH = 4**	**pH = 5**	**pH = 6**	**pH = 7**	**pH = 8**
–0.3 V	12.40	No deposit	No deposit	–	–	–
–0.4 V	30.81	100 % at. Mo	100 % at. Mo	–	100 % at. Mo	100 % at. Mo
–0.5 V	73.98	46.89	31.84	–	100 % at. Mo	100 % at. Mo
–0.6 V	28.35	49.27	33.59	0.11	100 % at. Mo	100 % at. Mo
–0.7 V	–	–	–	0.61	100 % at. Mo	100 % at. Mo
–0.8 V	–	–	–	1.34	100 % at. Se	100 % at. Mo
–0.9 V	–	–	–	0.55	100 % at. Se	100 % at. Se
–1.0 V	–	–	–	–	7.94	8.42
–1.1 V	–	–	–	–	37.00	100 % at. Mo

Oxygen analysis was not carried out due to limitations of the XRF method. When pH = 2 was applied, very brittle coatings were obtained. This is due to intensive hydrogen evolution and high internal stress appearing in the films (which flaked off during the process of electrolysis, therefore precluding the elemental analysis of the product). The quality of the deposited coatings was improved when the solutions with higher pH values were applied. When solutions with a pH from 3 to 5 were used, the layers were compact and well-adhered to the substrate, but only within the range of potentials from –0.4 to –0.6 V. The coatings were black in color. They consisted mostly of molybdenum (Tab. 1), even though selenium is more noble and should be deposited first. It can be assumed that, according to the Pourbaix diagram, the molybdenum ions are reduced to the oxides and deposited before selenium [30]:

$$MoO_4^{2-} + 2H_2O + 2e \rightarrow MoO_2 + 4OH^- \tag{4}$$

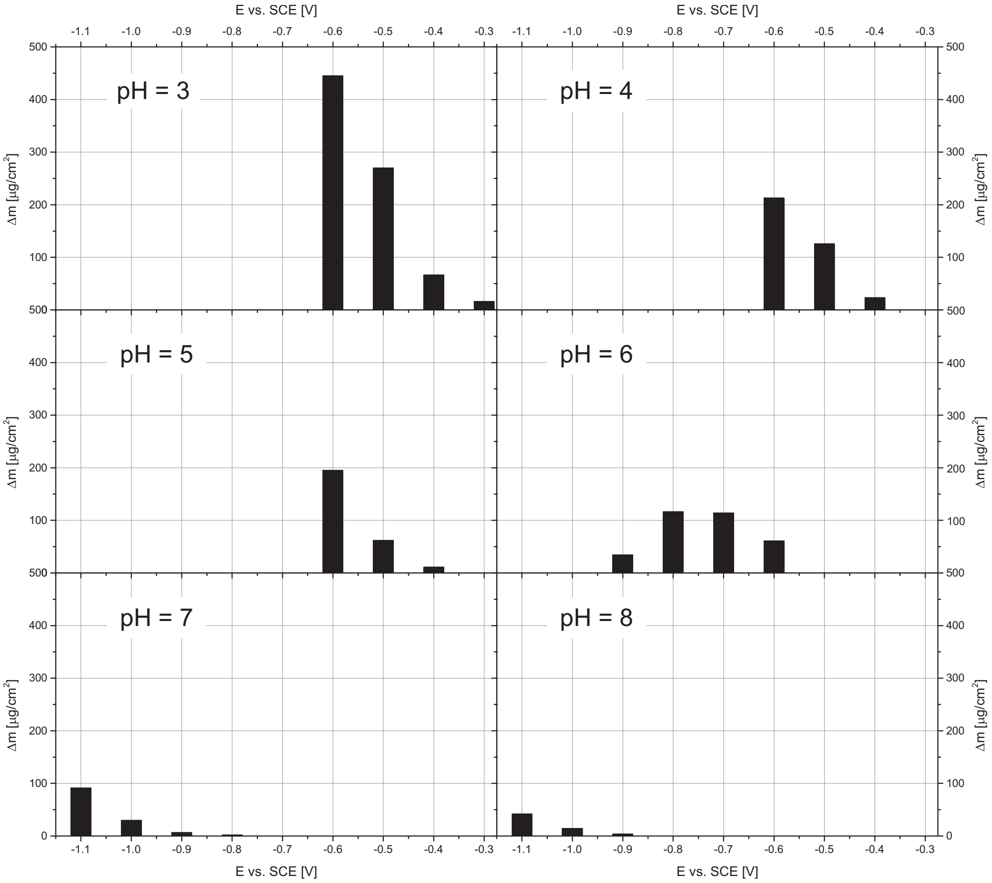

Fig. 1. The mass increase of the electrodes registered after deposition of coatings from electrolyte 0.05 M Na_2MoO_4, 0.002 M H_2SeO_3, 0.1 M Na_2SO_4, T = 55°C at different pH

The X-ray diffraction studies did not reveal any crystalline phases except copper substrate, so the presence of oxides was not confirmed. These results indicate that the obtained films were amorphous. Appling more-negative potentials caused the flaking off of the films from the electrode, similarly when an electrolyte with pH = 2 was used. The mass increment of the electrodes (Fig. 1) indicates that the rate of deposition was very fast and can be responsible for the appearance of internal stress in the deposits as well as its brittleness. Additionally, the process of hydrogen evolution was very intense when the acid pH and very-negative potentials were applied. These effects negatively impacted the quality of the deposits.

When a bath of pH = 6 was applied, the composition of the films changed significantly (Tab. 1). The higher content of selenium in the deposit was detected compared to the layers obtained at the same range of potentials but at a lower pH. The ratio between elements in the deposits is very close to the stoichiometry of molybdenum chalcogenides.

The further increasing of pH limits the possibility of deposition of Mo-Se coatings. There was no deposit when a more-positive potential than E = –0.7 V (in the case of pH = 7 and then E = –0.8 V at pH = 8) were applied. Below potential –0.7 V, an increment of the mass of the electrode was detected. The obtained films were very thin due to the low rate of chalcogenide deposition in the neutral and weak-alkaline pHs [10]. The films were composed mostly of selenium when more-positive potentials were applied, or in the majority of molybdenum in the case of applying more-negative potentials. There were no layers with intermediate composition close to the stoichiometry of molybdenum chalcogenides.

In order to determine the influence of deposition time on film composition, electrodeposition was performed by varying the deposition time from 5 to 60 minutes. The processes of electrolysis were conducted in the electrolyte at pH = 6 and at potential –0.8 V vs. SCE. The mass of the deposits increases with the time of electrolysis (Fig. 2), and all of the coatings were homogenous and well-adherent to the substrate. It is a very important issue that the coatings are compact and do not flake off when their thickness increases. The composition of the films slightly changed by decreasing molybdenum content in the range of 10% at. (Tab. 2). It is suggested that the mechanism of the co-reduction of molybdenum and selenium is not disturbed by the growth of semiconducting layers.

Table 2. Composition of the deposited coatings from electrolyte 0.05 M Na_2MoO_4, 0.002 M H_2SeO_3, 0.1 M Na_2SO_4, T = 55°C at different time of deposition

Time of deposition, [s]	**Mo/Se % at. ratio**
300	1.47
600	1.42
900	1.41
1800	0.93
3600	1.15

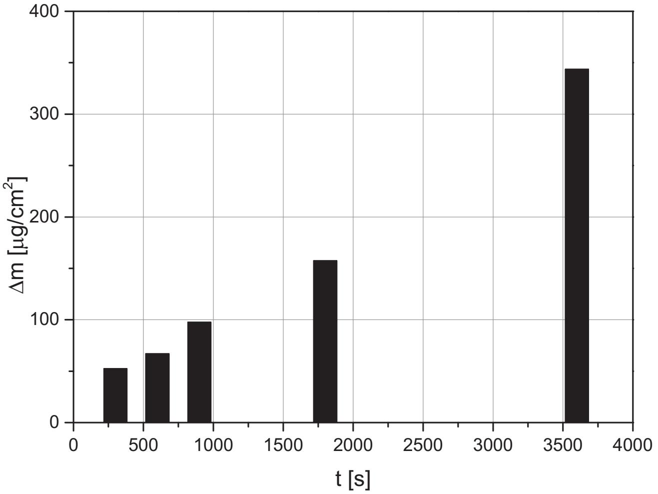

Fig. 2. The mass increment of the samples after deposition from electrolyte 0.05 M Na_2MoO_4*, 0.002 M* H_2SeO_3*, 0.1 M* Na_2SO_4*, T = 55°C at different time of deposition*

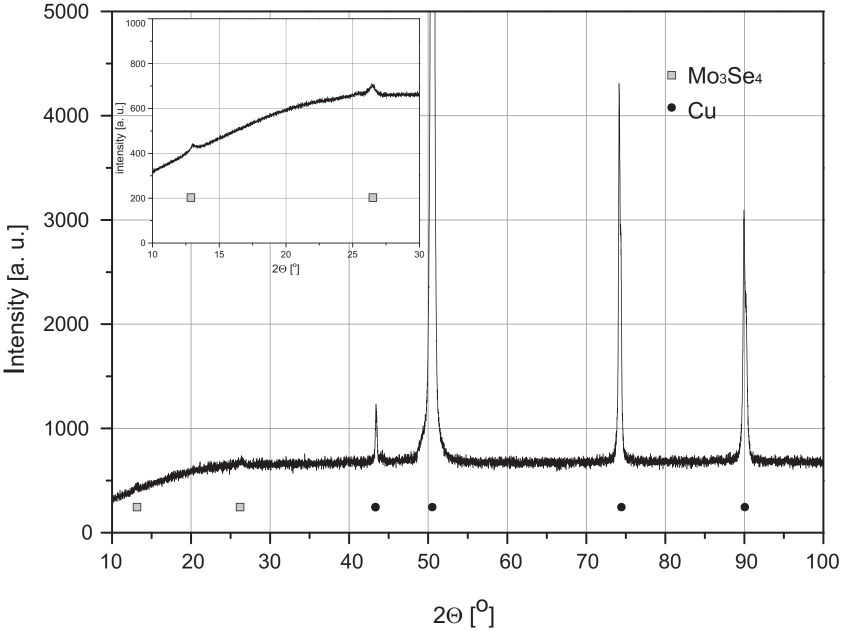

Fig. 3. XRD patterns of Mo-Se coatings deposited from electrolyte: 0.05 M Na_2MoO_4*, 0.002 M* H_2SeO_3*, 0.1 M* Na_2SO_4*, pH = 6, T = 55°C, at potential –0.6 V vs. SCE*

The selected X-ray diffraction (XRD) pattern of the electrodeposited coating on a copper substrate is shown in Figure 3. The phase analysis of the coatings was hindered.

The diffractogram mostly exhibits peaks related to the copper substrate (and only two very small peaks associated with the Mo_3Se_4 phase). This is due to the amorphous structure of the deposits [12]. This effect is characteristic for coatings obtained in the limiting current regime [24].

The surface morphology of Mo-Se thin films deposited at potential –0.6 V vs. SCE on copper substrate is shown in Figure 4. The as-deposited films have a homogenous and compact layer structure with no visible grain structure. It covers the copper substrate well without any cracks or pinholes. The characteristic flake-like structure is visible when a higher magnification is applied.

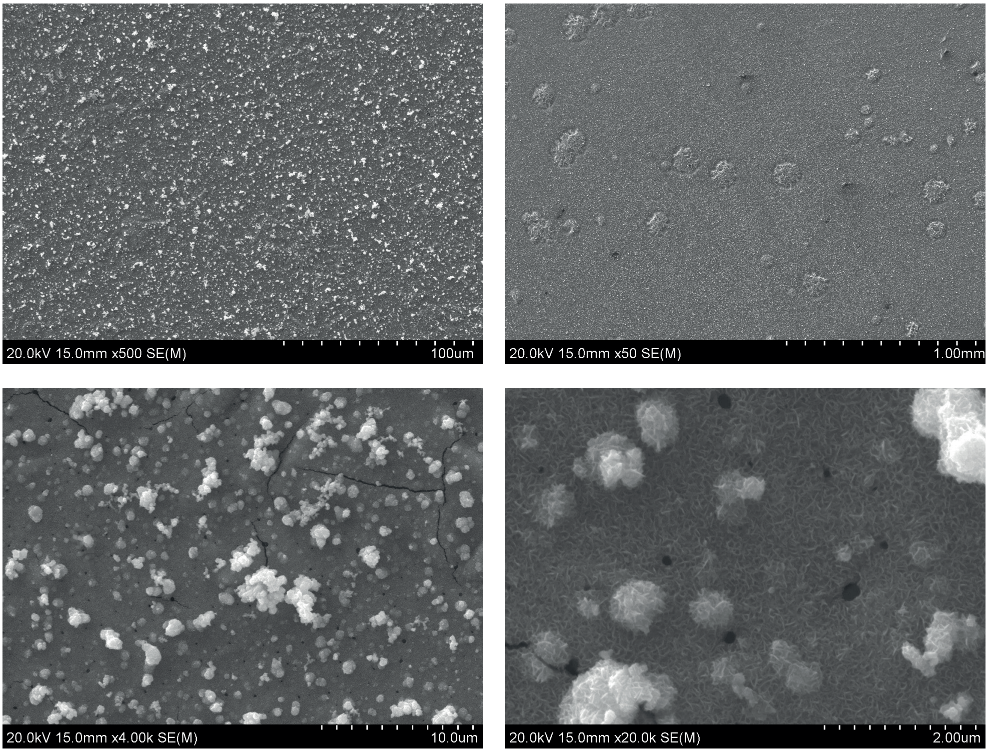

Fig. 4. The surface morphology of deposited layers obtained using Cu substrate. Bath composition: 0.05 M Na_2MoO_4*, 0.002 M* H_2SeO_3*,* $pH = 6$*,* $T = 55^{o}C$*, at potential –0.6 V vs. SCE*

4. Summary

It has been demonstrated that co-deposition of molybdenum and selenium is possible from a simple bath without the addition of any complex agents. The proper adjustment of the process of electrolysis has a crucial influence on the composition of the deposited films, and the very important factor is the pH of the electrolyte. When a pH below 6 is applied, the coatings consist mostly of molybdenum. Moreover, the coatings were very brittle when deposited at pH 2. The deposition of the coatings is possible at potentials below –0,8 V (when pH increased above 6), but the coatings consist mostly of pure selenium or molybdenum.

Synthesis of the films with a stoichiometry close to the molybdenum chalcogenides is limited to pH = 6 and is possible in a wide range of potentials (from –0.6 to –0.9 V). The obtained films characterize the amorphous structure and impede phase analysis. In consequence, further work is required that embraces a more-detailed phase analysis by XPS and conformation of the presence of selenide compounds or oxides (which is currently in progress in our laboratory).

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References

[1] Yang J., Shin H.S.: Recent advances in layered transition metal dichalcogenides for hydrogen evolution reaction. Journal of Materials Chemistry A, 2, 17 (2014), 5979–5985

[2] Pumera M., Sofer Z., Ambrosi A.: Layered transition metal dichalcogenides for electrochemical energy generation and storage. Journal of Materials Chemistry A, 2, 24 (2014), 8981–8987

[3] Chan K., Tsai C., Hansen H. A., Nørskov J. K.: Molybdenum sulfides and selenides as possible electrocatalysts for CO_2 reduction. Chemcatchem, 6, 7 (2014), 1899–1905

[4] Ponomarev E.A., Neumann-Spallart M., Hodes G., Lévy-Clément C.: Electrochemical deposition of MoS_2 thin films by reduction of tetrathiomolybdate. Thin Solid Films, 280, 1–2 (1996), 86–89

[5] Le Berre F., Tshimanga D., Guilloux A.L., Leclercq J., Sergent M., Peña O., Horyn R., Wojakowski A.: Rare-earth doping of the Mo_3Se_4 superconductor. Physica B: Condensed Matter, 228, 3–4 (1996), 261–271

[6] Aruchamy A.: Photoelectrochemistry and photovoltaics of layered semiconductors. Kluwer Academic, Dordrecht – Boston, 1992.

[7] Shariza S., Anand T.J.S.: Effect of deposition time on the structural and optical properties of molybdenum chalcogenides thin films. Chalcogenide Letters, 8, 9 (2011), 529–539

[8] Landolt D.: Electrodeposition science and technology in the last quarter of the twentieth century. Journal of the Electrochemical Society, 149, 3 (2002), S9–S20

[9] Mech K., Żabiński P., Mucha M., Kowalik R.: Electrodeposition of catalytically active Ni-Mo alloys. Archives of Metallurgy and Materials, 58, 1 (2013), 227–229

[10] Rajeshwar K.: Electrosynthesized thin films of group II–VI compound semiconductors, alloys and superstructures. Advanced Materials, 4, 1 (1992), 23–29

[11] Lincot D.: Electrodeposition of semiconductors. Thin Solid Films, 487, 1–2 (2005), 40–48

[12] Kowalik R., Zabiński P., Fitzner K.: Electrodeposition of ZnSe. Electrochimica Acta, 53, 21 (2008), 6184–6190

[13] Alkire R.C.: Advances in Electrochemical Science and Engineering, vol. 12. Wiley-VCH, Chichester, 2010

[14] Zabiński P., Mech K., Kowalik R.: Co-Mo and Co-Mo-C alloys deposited in a magnetic field of high intensity and their electrocatalytic properties. Archives of Metallurgy and Materials, 57, 1 (2012), 127–133

[15] Chandra S., Sahu S.N.: Electrodeposited semiconducting molybdenum selenide films. I. Preparatory technique and structural characterisation. Journal of Physics D: Applied Physics, 17, 10 (1984), 2115–2123

[16] Joseph Sahaya Anand T., Sanjeeviraja C., Jayachandran M.: Preparation of layered semiconductor ($MoSe_2$) by electrosynthesis. Vacuum, 60, 4 (2000), 431–435

[17] Dukstiene N., Kazancev K., Prosicevas I., Guobiene A.: Electrodeposition of Mo-Se thin films from a sulfamatic electrolyte. Journal of Solid State Electrochemistry, 8, 5 (2004), 330–336

[18] Delphine S.M., Jayachandran M., Sanjeeviraja C.: Pulsed electrodeposition and characterization of molybdenum diselenide thin film. Materials Research Bulletin, 40, 1 (2005), 135–147

[19] Dukstiene N., Tatariskinaite L.: Electrochemical examination of the influence of H_2SeO_3 on molybdenum electrodeposition on tin oxide electrode from aqueous citrate electrolyte. Polish Journal of Chemistry, 80, 10 (2006), 1715–1729

[20] Hahn B.P., Stevenson K.J.: Cathodic electrodeposition of mixed molybdenum-selenium oxides. Journal of Electroanalytical Chemistry, 638, 1 (2010), 151–160

[21] Kröger F.A.: Cathodic deposition and characterization of metallic or semiconducting binary alloys or compounds. Journal of the Electrochemical Society, 125, 12 (1978), 2028–2034

[22] Gawęda S., Kowalik R., Kwolek P., Macyk W., Mech J., Oszajca M., Podborska A., Szaciłowski K.: Nanoscale digital devices based on the photoelectrochemical photocurrent switching effect: Preparation, properties and applications. Israel Journal of Chemistry, 51 (2011), 36–55

[23] Baker H.: Alloy phase diagrams. Materials Park, Ohio, ASM International, 1992

[24] Kowalik R., Fitzner K.: About the conditions of zinc selenide electrodeposition from aqueous solutions. Metallurgy and Foundry Engineering, 30, 2 (2004), 140–141

[25] Kowalik R., Fitzner K.: Analysis of the mechanism for electrodeposition of the ZnSe phase on Cu substrate. Journal of Electroanalytical Chemistry, 633, 1 (2009), 78–84

[26] Kowalik R., Szaciłowski K., Zabiński P.: Photoelectrochemical study of ZnSe electrodeposition on Cu electrode. Journal of Electroanalytical Chemistry, 674 (2012), 108–112

[27] Pourbaix M.: Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon, New York, 1966

[28] Pope M.T.: Heteropoly and isopoly oxometalates. Springer-Verlag, Berlin – New York, 1983

[29] Bouroushian M.: Electrochemistry of metal chalcogenides. Springer, Berlin, 2010

[30] Nuñez M.: Metal electrodeposition. Nova Science Publishers, New York, 2005

[31] Podlaha E.J., Landolt D.: Induced codeposition. III. Molybdenum alloys with nickel, cobalt, and iron. Journal of the Electrochemical Society, 144, 5 (1997), 1672–1680

[32] Podlaha E.J., Landolt D.: Induced codeposition: I. An experimental investigation of Ni-Mo alloys. Journal of the Electrochemical Society, 143, 3 (1996), 885–892