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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**ELECTROCHEMICAL SYNTHESIS AND STUDY OF
THE PROPERTIES OF MoS₂ SEMICONDUCTOR THIN
FILMS**

Speciality: 2308.01 Electrochemistry
2303.01 Inorganic chemistry

Field of science: Chemistry

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Baku – 2021

The dissertation work was performed in the laboratory of "Nanoelectrochemistry and Electrocatalysis" of the Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev of ANAS.

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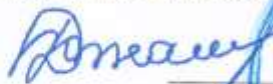
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GENERAL FEATURES OF THE RESEARCH WORK

The relevance and scientific elaboration of the topic. Modern stages of development in the world economy are characterized by the increased contribution of the population of underdeveloped and developing countries to industrial production. In this context, the increase in living standards is accompanied by an increase in energy consumption. The rapid increase in energy consumption threatens the depletion of natural energy resources. At the same time, more environmental pollution with products of fuel combustion, climate changes in the planet due to the greenhouse effect, the direct influence of the sun's ultraviolet and gamma rays on Earth as a result of loss of the Earth's ozone layer create global problems for humanity. This damages atmosphere, plantations, water bodies and etc. It is great losses that preventing pollution by natural physicochemical and microbiological methods through the processing of pollutants and nature's renewal is no longer possible.

In light of the above, the widespread practical use of environmentally friendly and non-traditional, and renewable energy sources that do not pollute the environment is becoming progressively important. Such sources include solar energy, wind energy, sea wave energy, biomass energy, geothermal energy and etc. The nature, use, and application of each of these energy sources are significantly different. It is also important to collect and store converted electricity or chemical energy.

Thin semiconductor films used in energy converters and their production is one of the fastest growing promising technologies in the 21st century. Metal chalcogenides have a special place among these semiconductors. Sulfur compounds with unique optical and electronic properties have been the basis of micro- and optoelectronics for decades. Thin films of sulfur compounds are widely used as photodetectors, photoluminescent materials, thermoelectric materials, solar cells, decorative coatings, sensor materials and etc. One such sulfur compound is MoS₂.

MoS₂ is a stable, layered semiconductor with photosensitive properties and n-type conductivity in the visible region of the spectrum. Due to the width of the bandgap (1.7 eV), it can be successfully used as a photoelectrode material in solar cells and hydrogen production. Recent research shows that MoS₂ nanoparticles are a cheaper alternative to

platinum in the electrochemical and photochemical generation of hydrogen from water.

There are various methods for obtaining the chemical compound MoS₂ at present. However, to achieve the set goal in the presented research work, the electrochemical method that is more promising method has been used.

The aim and tasks of the study. The main aim of the dissertation is to obtain thin layers of Mo-S semiconductor from aqueous solutions by electrochemical methods and to study the electrophysical and photophysical properties of the obtained thin layers. Thus, the research study includes the following steps.

- To clarify the mechanism and kinetics of the electrolytic deposition process of both molybdenum and sulfur separately and together.

- To study the effect of various factors (temperature, electrolyte composition, acidity, electrode materials, etc.) on the process of joint electrolytic deposition of molybdenum and sulfur.

- To determine the electrophysical and photoelectrochemical properties of thin layers of electrochemically obtained chemical compound MoS₂.

Research methods. The research corresponding to the topic of the dissertation was carried out using modern methods of analysis, such as X-ray phase analysis, scanning electron microscope, Raman combination scattering analysis, potentiodynamic, potentiostatic, galvanostatic, electrochemical, and photoelectrochemical studies. X-ray phase analysis of samples has been accomplished in “D2 Phazer” diffractometer from the German company Bruker, morphology, relief and chemical element composition of samples –in scanning microscope branded “Carel Zeiss Sigma”, the combined scattering (Raman spectroscopy) – using 3D Confocal Raman System, Micro-NanoScale Microspectroscopy, Nanofinder 30 (Tokyo Instr., Japan). The polarization curves of deposition processes were plotted using the IVIUMSTAT Electrochemical Interface potentiostat.

The main provisions of the dissertation.

- ✓ Electrochemical co-deposition of molybdenum and sulfur from an aqueous electrolyte has been accomplished. The nature of polarization during the separate electroreduction process of molybdenum and sulfur was investigated and it was found that the deposition of molybdenum on the platinum electrode in the potential range of 0.47 - (-0.8) V occurs

gradually, the nature of polarization is the first electrochemical and then accompanied by concentration polarization. The processes of electroreduction of sulfite and thiosulfate ions proceed in the potential range of 0.4 - (-0.7) V on the Pt electrode and 0.1 - (-1.0) V on the Mo electrode. The kinetics of the reduction process is accompanied by electrochemical polarization.

✓ The process of electrolytic co-deposition of molybdenum and sulfur from aqueous solutions on different electrodes (Pt and Ni) has been studied by recording cyclic and cathodic polarization curves. It was found that, depending on the material of the electrode, along with the change in the rate of the electrochemical reaction, the potential field of joint deposition also differs significantly. Thus, the process of co-deposition of molybdenum and sulfur on platinum electrodes takes place at a potential of -0.5 - (-0.65)V, while on the Ni electrode this process occurs at a potential of -0.55 - (-1.0)V.

✓ The effect of various factors (current density, temperature, total concentration, the concentration of components, etc.) on the composition of deposited thin Mo-S layers from an aqueous solution has been studied; electrolyte composition was determined for electrochemical obtaining thin semiconducting layers corresponding to stoichiometric composition (MoS_2); the proper condition for electrolysis was selected, (mol/L): 1.0 MNa_2MoO_4 +0.1 M Na_2SO_3 , current density $i_k = 7\text{A/dm}^2$, $T= 338\text{K}$. Anode - platinum, cathode - platinum, nickel.

✓ A regression equation was created by statistical planning of experiments for obtaining thin layers of molybdenum-sulfur by electrochemical deposition way from molybdate and sulfite electrolytes.

✓ The morphology, chemical composition, and structure of the Mo-S thin layers obtained by electrochemical methods were studied by scanning electron microscopy, X-ray phase, and Raman spectroscopy. As a result of the research, it was found that as a consequence of electrolytic deposition from the aqueous solution, the chemical compound Mo_3S_4 is also formed on the surface of the cathode along with the fine crystalline MoS_2 .

✓ The semiconductor properties of electrochemically obtained Mo-S thin films were studied and it was determined that they have an "n" type conductivity. The temperature dependence of the electrical conductivity of the obtained layers and a number of semiconductor constants were calculated (temperature sensitivity coefficient - B,

activation energy of electrical conductivity - ΔE , band gap energy, etc.). The obtained values show that the low value of electrical resistance and temperature coefficient of thin layers of MoS_2 allows these compounds to use them in electronics.

✓ The chronoamperometric and chronopotentiometric curves recorded for the study of the photoelectrochemical properties of electrochemically synthesized Mo-S thin films show that the MoS_2 semiconductor compound besides n-type conductivity has also a photosensitivity property. This allows the use of electrochemically deposited thin layers of MoS_2 with a bandwidth of $E_g=1.41$ eV, calculated by us, as one of the components in the range of visible light in photoelectronic and new-generation solar cells.

Scientific innovation of the study. The scientific innovation of the dissertation is the study of the basic regularities of the joint electrolytic deposition of molybdenum and sulfur from an aqueous electrolyte by electrochemical deposition and the obtaining semiconductor thin layers of MoS_2 in accordance with the stoichiometric composition.

The theoretical and practical significance of the research. The practical significance of the dissertation is based on obtaining a chemical compound with a stoichiometric composition of MoS_2 , electrochemically deposited in the form of a thin layer, which can be applied in semiconductor technology on various metal electrodes and finding the utilization areas of these films in solar panels and in the process of obtaining hydrogen from water as photoelectrode material.

Approbation and application. The materials of the dissertation were presented at the following international scientific conferences: "Scientific conference dedicated to the 90th anniversary of Academician T.N.Shakhtakhtinsky", (2015) Baku, "Alternative sources of raw materials and fuel" IV International Scientific and Technical Conference (2015) Minsk, Belarus «International Conference on Chemical Sciences & Applications» 2016, Alex. Egypt, «5th International Caucasian Symposium on Polymers & Advanced Materials» (2017), Tbilisi, Georgia, «Chemistry, chemical technologies, and ecology: science, production, education» International scientific-practical conference and school for young students, (2018) Dagestan, Scientific conference "Nagiyev readings" dedicated to the 110th anniversary of Academician M. Nagiyev, (2018) Baku, International Scientific and Technical

Conference "Modern Electrochemical Technologies and Equipment-2019", (2019), Minsk, Belarus.

The main content of the dissertation has been published in 16 scientific articles. 9 of them are the article (5 articles in the database of Web of Science) and 7 are theses.

Name of the research organization of dissertation work. The dissertation work has been performed in the laboratory of "Nanoelectrochemistry and electrocatalysis" of the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev of ANAS.

Volume and structure of the dissertation. The dissertation consists of an introduction (12744 characters), 4 chapters (148 262 characters), general results (3480 characters), and a list of references (33277 characters). The volume of the dissertation is 139 pages (206706 characters) of computer text. The dissertation has 52 figures, 4 tables, and 215 references. The volume of the dissertation is 168111 characters, excluding pictures, tables, graphs, and list of reference.

The main content of the work

The actualness of the dissertation topic and the aim of the work, innovation of the obtained results, scientific and practical significance have been demonstrated in **the introduction**.

The first chapter provides literature about electrochemical obtaining thin layers of MoS₂ semiconductors and the analysis of the studied properties of the obtained layers. This information was used to summarize the results of the research [1, 3, 14].

The second chapter of the dissertation is devoted to the description of reagents, devices, and research methods used in the investigation.

Potentiostatic deposition of Mo-S thin layers was carried out in a three-electrode glass cell using a computer-equipped IVIUMSTAT Electrochemical Interface potentiostat. Electrodes used in the work: 1) working electrode - cathode, the auxiliary electrode – anode, and reference electrode. A platinum plate with a surface area of 4 cm² was used as an auxiliary electrode, Ni plate with a surface area of 2 cm², Mo wire with a surface area of 2.04·10⁻²cm², and a Pt wire with a surface area of 0.4 cm² were used as a working electrode. Silver/silver chloride (Ag / AgCl / KCl) was used as a comparison electrode.

The surface of the obtained thin films was investigated by Scanning Electron Microscopes, optical properties by SPECORD-250-222P

spectrophotometer, electrical properties by 4-point probe surface resistance measurement, and thickness by MII-4 optical interferometer.

Surface analysis, morphology, relief, and chemical element composition of electrodes modified with electrochemically deposited thin layers of Mo-S were carried out at Scanning Electron Microscope SEM (Japan) of “Carl Zeiss Sigma” at an acceleration voltage of 15 keV and an operating distance of 4-5 nm.

Phase analysis of MoS₂ thin films was performed using a “D2 Phazer” diffractometer (CuK_α- radiation, Ni-filter) from a German “Bruker” company.

The temperature dependence of the electrical conductivity of Mo - S thin layers has been studied by E6-10 Ohmmeter, Volt-Ampere characteristic has been determined using the static characteristic.

Combination scattering of Mo-S samples obtained on the Ni electrode has been recorded (Raman spectroscopy) by 3D Confocal Raman System, Micro-NanoScaleMicrospectroscopy, Nanofinder 30 (Tokyo Instr., Japan) with Neodymium YAG - Laser beams with an excitation wavelength of $\lambda = 532$ nm.

The third chapter presents the results of the study of the joint electrodeposition process of thin layers of semiconductor MoS₂. In order to carry out this process by electrochemical method, first of all, the electrochemical reduction process of the initial components from the selected electrolyte must be studied. First, the study of the process of electroreduction of molybdate anions from an aqueous electrolyte (Na₂MoO₄·2H₂O + H₂O) was carried out on the cathode [2, 4].

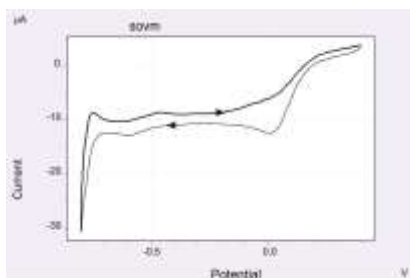
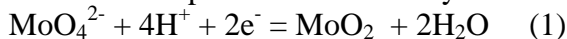


Figure 1. Cyclic polarization curve of molybdate ions on the platinum electrode in aqueous medium. Electrolyte (M): 0.25 Na₂MoO₄ + H₂O. T= 295 K; eV = 20 mV/sec.

Figure 1 shows the cyclic polarization curve of the electrochemical reduction process of molybdate ions in the aqueous medium.

As is seen from the figure, the electroreduction process of molybdate ions in this medium is gradual at potential values of 0.25 - (-0.8) V. The nature of the peaks that occur during the process can be explained using information about the standard potentials of these systems:



That is, part I of the polarization curve (up to -0.1V potential) corresponds to reaction (1), and a limit current is observed from this potential to -0.48 V potential. In the next stage of the process, part II (-0.48 - (-0.65) in the V potential range) is accompanied by reaction (2). After a potential of -0.65 V, a process takes place corresponding to reaction (3), in which a layer of metallic molybdenum is deposited on the surface of the electrode. This can also be observed by changing the color of the electrode surface to light brown. To determine the nature of cathode polarization, the temperature-kinetic method was applied in the potential range of polarization curves 0.2 - 0.7 V.

The results show that the cathode process is electrochemical in nature. That is, in this case, the speed of the cathode process is limited by the diffusion of uncharged ions on the electrode surface.

The process of electrochemical reduction of molybdate ions was also studied in tartrate electrolytes for comparison (Figure 2).

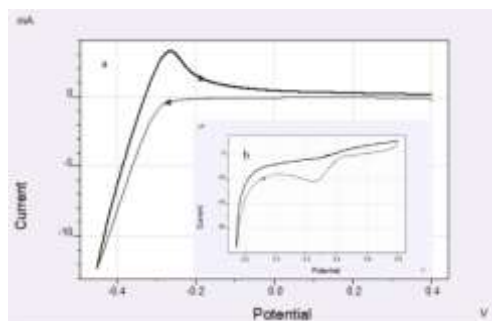
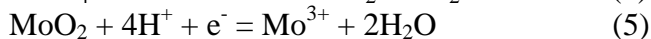
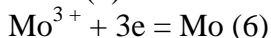


Figure 2. Cyclic polarization curves of the electroreduction process of molybdate ions in tartrate solutions on the Pt electrode. Electrolyte (M): 0,1 Na₂MoO₄·2H₂O + 0,007 C₄H₆O₆. T = 293 K, E_v=0.02 V/s. a - general process, b - initial stage

As is seen from the figure, the electrochemical reduction of molybdate ions on the cathode occurs gradually in the potential range of 0.47 - (-0.25) V. In our opinion, the reduction process in the potential range of 0.47 - (0.25) V follows the reaction (4) (Figure 2.b), and in the potential range of 0.27 - 0.0 V the reaction (5) (Figure 2.b):



Then, starting from the potential of 0.0 V, Mo^{3+} ions are completely reduced to the metal by the reaction (6):



As in the aqueous solution, the kinetics of the electroreduction process from the tartrate-added electrolyte was studied in the potential range of 0.0 - (-0.25) V. It was found that the electroreduction of molybdate ions from tartrate-added electrolytes is accompanied by mixed kinetics.

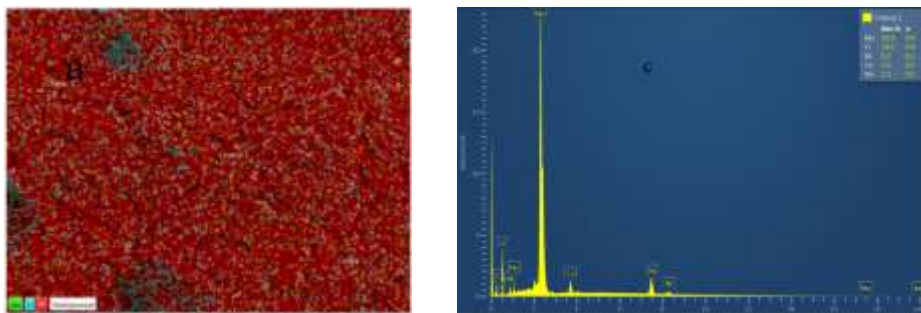


Figure 3. SEM (a, b) and EDAX (c) images of Mo deposited on the surface of the Ni electrode. Electrolyte (M): 0,1 $\text{Na}_2\text{MoO}_4 \times 2\text{H}_2\text{O}$ + 0,007 $\text{C}_4\text{H}_6\text{O}_6$. T = 293 K, $E_v = 0,02 \text{ V s}^{-1}$

Figure 3 shows scanning electron microscopy images of the deposited molybdenum layer. The results show that the deposition of molybdenum during the process is 63%.

The comparison of electroreduction processes in electrolytes with the addition of aqueous and tartaric acid shows that the high concentration of hydrogen ions in tartrate solutions leads to start the reduction process at more positive potentials (0.47V) (pH = 2.0-2.5). However, in aqueous solutions (pH = 5.0-5.5) electroreduction occurs at a potential of 0.2 V.

Since the purpose of our study is to carry out the process of co-deposition of molybdenum and sulfur, it is convenient for us to take place the reduction of the molybdate ions at more negative potentials to achieve a reduction of sulfur to the S^{2-} ion. From this point of view, it is advisable to carry out the research in aqueous solutions.

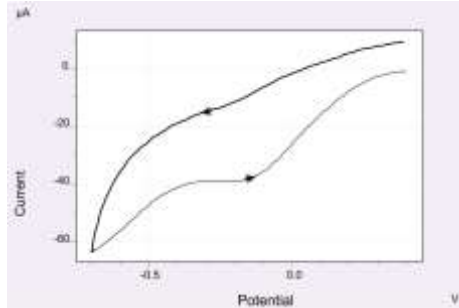


Figure 4. Cyclic polarization curve of the electroreduction of thiosulfate ions on Pt cathode. Electrolyte (mol / L): 0.1 $Na_2S_2O_3$, $E_V=0,03$ V/san, $T= 298$ K

The electrochemical reduction process of thiosulfate ions in an aqueous medium on the cathode was also studied (Fig. 4). Electroreduction on Pt occurs at a potential of 0.4 - (-0.7) V [6].

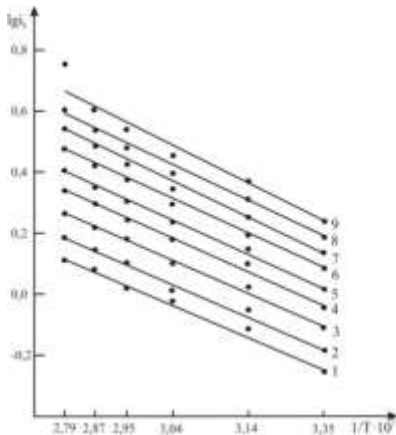


Figure 5. The function between $lg i_k - 1/T$. 1- (-0.2)V, 2- (-0.25)V, 3- (-0.3)V, 4- (0.35)V, 5- (-0.4)V, 6- (-0.45)V, 7- (0.5)V, 8- (0.55)V, 9- (-0.6)V

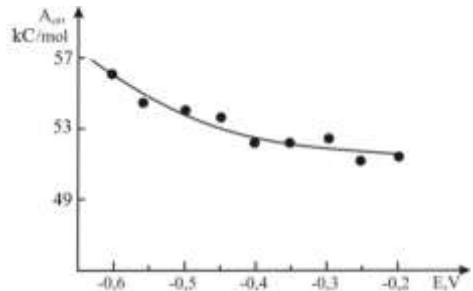


Figure 6. The potential dependence of effective activation energy

Based on the recorded polarization curves, the effective activation energy (A_{ef}) of the reduction process taking place on the cathode was calculated and the nature of the polarization was determined (Fig. 5, 6).

The process of electrochemical reduction of sulfite ions in an aqueous medium has been studied on Pt and Ni electrodes.

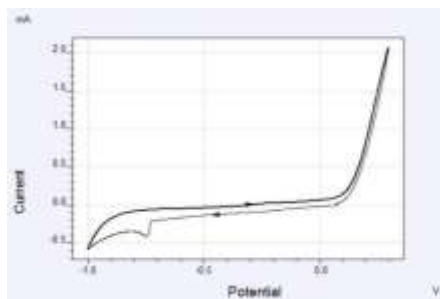
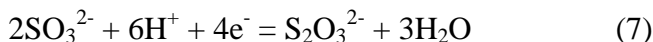


Figure 7. Cyclic polarization curve of the electroreduction process of sulfite ions at the Pt electrode. Electrolyte (mol/l): 0.1 Na_2SO_3 , $E_V = 0.03 \text{ V/sec}$, $T = 298 \text{ K}$.

As can be seen from Figure 7, during the electroreduction process of sulfite ions on the Pt electrode, up to the potential value of 0.7V occurs reduction the SO_3^{2-} ion up to the $\text{S}_2\text{O}_3^{2-}$ ion formed by the dissociation of Na_2SO_3 .



After -0.72V potential, the reduction of $\text{S}_2\text{O}_3^{2-}$ ion continues according to the following reaction:

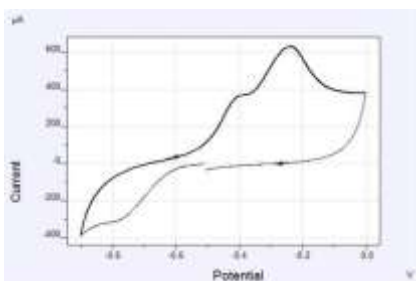
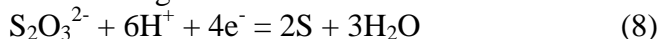
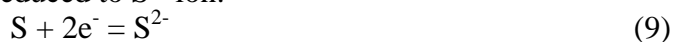


Figure 8. Cyclic polarization curve of the electroreduction process of sulfite ions at the Ni electrode. Electrolyte (mol/l): 0.1 Na_2SO_3 , $E_V = 0.03 \text{ V/sec}$, $T = 298 \text{ K}$.

Starting from the value of -0.75V potential, the resulting sulfur is completely reduced to S^{2-} ion:



This can also be seen visually by transforming the surface of the Pt electrode yellowish.

As can be seen from Figure 8, the reduction of sulfite ions on the Ni electrode compared to Pt occurs by the same mechanism at a potential of $-0.55 - (-0.9)$ V. That is, the potential range of $-0.55 - (-0.75)$ V corresponds to the complete reduction of $S_2O_3^{2-}$ ion to S, and the region after -0.75 V to S^{2-} ion.

After determining the potential reduction area of sulfite ions from the aqueous solution, was studied the effect of temperature, which is an important factor in the process.

Wherein, the studies were conducted in the temperature range of 298 - 348 K (Figure 9).

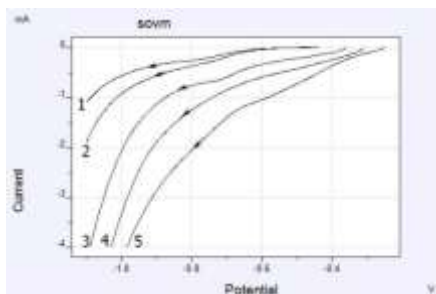


Figure 9. The effect of temperature on the electroreduction process of sulfite ions on the Pt electrode. Electrolyte (mol/l): 0.1 $Na_2S_2O_3$. Temperature (K): 1- 298; 2- 318; 3- 328; 4- 338; 5- 348. $E_v = 0,03$ V/sec.

Figure 9 shows that the electroreduction process of sulfite ions becomes easier with increasing temperature, that is, the stationary potential of the electrode moves towards a positive direction. Thus, while the potential of the stationary electrode at 298 K is -0.43 V, at 348 K this potential is -0.25 V.

A comparison of the electroreduction of both sulfite and thiosulfate solutions shows that in the case of sulfite ions, the first SO_3^{2-} ion is reduced to the $S_2O_3^{2-}$ ion, and the latter to free sulfur. At more negative (-0.75 V) values of the cathode potential, occurs the process $S + 2e^- \rightarrow S^{2-}$ takes place. It should be noted, that the process of electroreduction of $S_2O_3^{2-}$ ions to free sulfur is easier than SO_3^{2-} ions. Therefore, when using thiosulfate electrolyte in the process of obtaining thin layers of MoS_2 by galvanostatic method, it was determined that in the composition obtained

MoS₂ contains free sulfur. This is due to the fact that the reduction of sulfite ions in free sulfur is faster than the process of electroreduction of free sulfur into sulfide ions, as a result of which the free sulfur formed on the electrode surface can not be reduced to end to S²⁻ ions and remains in the resulting thin layer. That is why it is more expedient to use sulfite electrolyte as a source of sulfur for electrochemical precipitation of thin layers of MoS₂.

Co-electrochemical deposition of Mo [4, 7] and sulfur [6] was carried out in an aqueous medium. Analysis of the polarization curves shows that the co-deposition process occurs at more positive potential.



According to figure 10, the electrochemical deposition process on the Pt electrode is carried out in stages within the potentials of 0.5 - (-0.65)V by the following reactions:

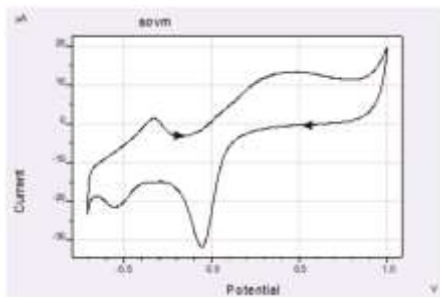


Figure 10. Cyclic polarization curve of the co-deposition process of molybdenum and sulfur in aqueous electrolyte on the Pt electrode. Electrolyte (M):1 Na₂MoO₄·2H₂O + 0.1 Na₂SO₃. T = 298K. $\nu_{sc} = 0.02$ V/sec

Starting from the 0.5V potential to a potential of -0.3V, electrochemical deposition of sulfur on the surface of the Pt electrode occurs (12). This is followed by the joint electrochemical deposition of molybdenum and sulfur (13) in the potential range of -0.3 - (-0.65) V. In this case, the surface of the electrode is covered with a black layer [6]. The continuation of the process is described in the anode part of the cyclic curve. Here, the peak corresponding to the potential of -0.3 V

refers to the dissolution of the formed Mo-S layer, and the peak corresponding to the potential of 0.2 - 0.1V to free sulfur. The study of the co-deposition process up to a potential of -0.7 V is due to the fact that after this potential hydrogen is released. This prevents further study of the co-deposition process [8, 9].

The process of electrolysis of molybdenum with sulfur was also investigated on a nickel electrode. As can be seen from Figure 11, deposition on the Ni-electrode occurs in the potential range of -0.55 - (-1.0) V, more in the direction of the cathode, in comparison with the Pt-electrode [9].

After determining the electrolysis potential of molybdenum with sulfur, the next stage of the study was devoted to the choice of the optimal electrolyte and electrolysis conditions for obtaining the chemical compound MoS₂ with stoichiometric composition. For this purpose, the influence of various factors on the co-deposition process has been studied.

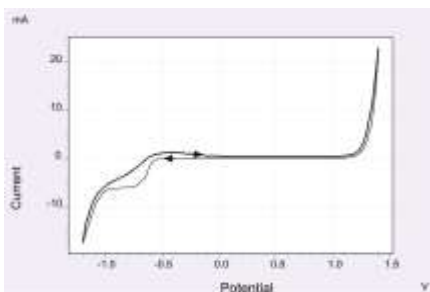


Figure 11. The cyclic polarization curve of the joint electro-deposition process of Mo and S in an aqueous medium on the Ni electrode. Electrolyte (M): 1 Na₂MoO₄·2H₂O + 0.1 Na₂SO₃. T = 338K, E_V=0,03 V/sec.

At this stage of the study, the effect of the concentrations of molybdate ions and sulfite ions was studied separately by potentiodynamic method.

The recorded polarization curves show that as the concentration of molybdate ions increases, the electrodeposition potential shifts towards the cathode [10]. It also affects the composition and quality of the obtained Mo-S thin layers. Table 1 shows the results of the experiments. As can be seen from the table, black, smooth, crystalline, evenly distributed on the surface films are obtained when the concentration of

molybdate ions in the electrolyte is 1.0 M. After this value of concentration, the quality of the obtained thin films deteriorates and their composition deviates from stoichiometry.

Table 1

The influence of concentration of molybdate ions on the composition and quality of electrochemically deposited Mo-S thin films

	Electrolyte content, (M)		Amount of Mo in the layers, %	Apperance of the layers
	Na ₂ MoO ₄ ·2H ₂ O	Na ₂ SO ₃		
1.	0.1	0.1	21.6	Black, uneven, amorphous, rough
2.	0.2	0.1	33.2	Black, uneven, polycrystalline, rough
3.	0.4	0.1	42.8	Black, amorphous, even, smooth
4.	0.8	0.1	54.3	Black, even, amorphous, smooth
5.	1.0	0.1	60.1	Black, smooth, crystalline, even
6.	1.2	0.1	65.3	Black, crystalline, uneven, rough

Therefore, 1.0-1.1 M concentration was chosen as the optimal concentration interval of molybdate ions [7, 12]. The effect of the concentration of sulfite ions on the co-deposition of molybdenum and sulfur was studied in the concentration range of 0.01-0.2 M. As the concentration of sulfite ions in the electrolyte increases, the deposition potential shifts to the direction of the cathode (from 0.15 V to 0.35 V). There are also changes in the composition and quality of Mo-S deposits obtained by changing the concentration of sulfite ions.

Table 2

The influence of sulfite ion concentration on the composition and quality of electrochemically deposited Mo-S thin films

№	Electrolyte content, (M)		Amount of Mo in the layers, %	Apperance of the layers
	Na ₂ SO ₃	Na ₂ MoO ₄ ·2H ₂ O		
1.	0.01	1	11.7	Black, even, amorphous, rough
2.	0.02	1	19.2	Black, even, amorphous, smooth

3.	0.04	1	26.4	Black, amorphous, even, smooth
4.	0.08	1	32.1	Black, uneven, polycrystalline, rough
5.	0.1	1	39.9	Black, smooth, polycrystalline, even
6.	0.2	1	59.3	Black, polycrystalline, uneven, rough

As can be seen from table 2, when the concentration of sulfite ions in the electrolyte is 0.1 M, black smooth crystalline Mo-S layers are formed, corresponding to the stoichiometric composition and evenly distributed over the electrode surface.

The effect of temperature on the co-deposition process was studied at 298-348K [11]. The results show that the joint deposition potential of Mo-S shifts to the positive direction with increasing electrolyte temperature. In addition, changes in temperature also affect the adhesion of the deposited Mo-S layers to the electrode, and the adhesion deteriorates above $T = 338$ K. Therefore, the optimum temperature range 333-338 K was taken to obtain black, smooth, crystalline thin Mo-S layers evenly distributed on the surface and corresponding to the stoichiometric composition.

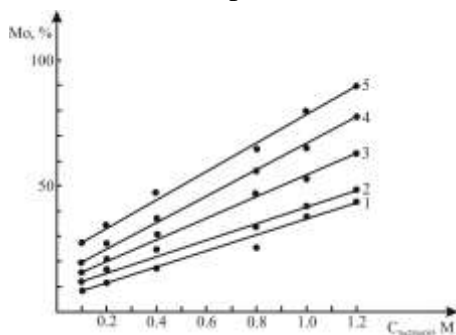


Figure 12. The effect of changing in Na_2MoO_4 concentration on the amount of Mo in deposits content of cathode. Electrolyte (M): 1.0 Na_2MoO_4 + 0.1 Na_2SO_3 . Current density (mA/cm^2): 1- 2.8; 2- 3.2; 3- 5; 4- 7; 5- 9. $T=338\text{K}$.

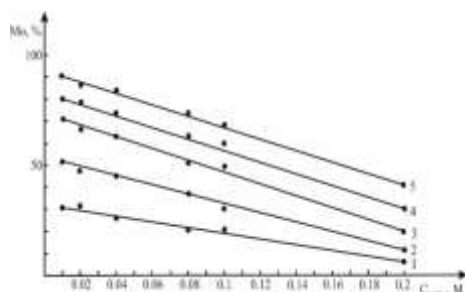


Figure 13. The effect of Na_2SO_3 concentration on the amount of Mo in the deposited layers. Electrolyte (M): 1.0 Na_2MoO_4 + Na_2SO_3 . Current density (mA/cm^2): 1- 2.8; 2- 3.2; 3- 5; 4- 7; 5- 9. $T=338\text{K}$.

The effect of various factors on the composition of deposits formed during the deposition process was also studied by galvanostatic method [7, 9, 12].

Figure 12 shows the effect of changes in the concentration of Na_2MoO_4 in the range of 0.1-1.2 M on the amount of Mo in the cathode deposition. As is seen from the figure, as the concentration of Na_2MoO_4 in the electrolyte increases, the amount of Mo in the obtained cathode deposits increases.

The increase in concentration also improves the quality of the deposits and their adhesion to the electrode surface.

An increase in current density also causes an increase in the amount of Mo in the cathode deposits. However, when the value of the current density exceeds $7\text{mA}/\text{cm}^2$, the quality of the deposited layers deteriorates and deviations from the stoichiometric composition occur. Therefore, values of Na_2MoO_4 concentration of 1.0M and current density of $7\text{mA}/\text{cm}^2$ were selected as optimal conditions.

An increase in the concentration of Na_2SO_3 in the electrolyte from 0.01 M to 0.2 M at different current densities (Figure 13) shows that the amount of Mo in the deposited layers decreases from 91.2% to 7.1%. Stoichiometric Mo-S layers are formed at a current density of $7\text{mA}/\text{cm}^2$ and at 0.1 M concentration of Na_2SO_3 .

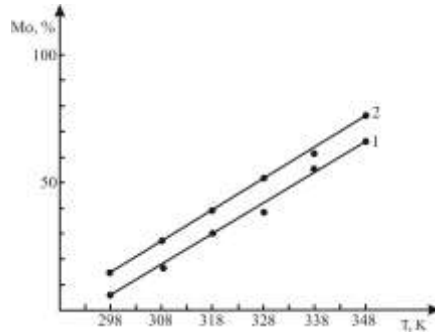


Figure 14. The effect of temperature on the amount of Mo in the deposited layers. Electrolyte (M): 1.0 Na_2MoO_4 + 0.1 Na_2SO_3 . Current density (mA / cm^2): 1-5; 2- 7.

The effect of one main factor – of temperature on the amount of Mo in the depositing layers was studied in the range 298-348 K (Figure 14). As is seen from the figure, as the temperature of the electrolyte increases, the amount of Mo in the deposited layers increases and the quality of the

layers also changes. The results show that evenly distributed, black Mo-S layers are obtained on a glossy surface when the electrolyte temperature is 338 K. The subsequent increase in the temperature was inducted as the optimal temperature range 333-338 K, as it caused the formation of unevenly distributed, rough and poor adhesion to the cathode surface.

The effect of current density on the amount of Mo in the cathode deposits was studied at different concentrations of Na_2MoO_4 in the range of 2.8 - 9 mA/cm^2 (Figure 15).

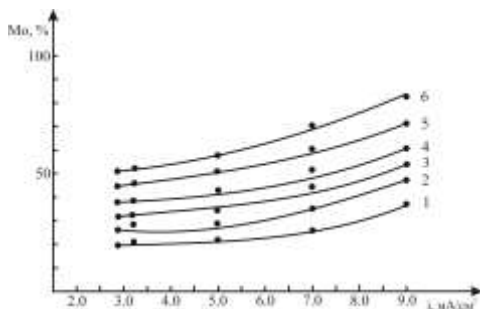


Figure 15. The effect of current density on the amount of Mo in cathode deposits.

T = 338K, Electrolyte (M):

- | | |
|---|---|
| 1. $0.2\text{Na}_2\text{MoO}_4 + 0.1\text{Na}_2\text{SO}_3$ | 4. $0.8\text{Na}_2\text{MoO}_4 + 0.1\text{Na}_2\text{SO}_3$ |
| 2. $0.4\text{Na}_2\text{MoO}_4 + 0.1\text{Na}_2\text{SO}_3$ | 5. $1.0\text{Na}_2\text{MoO}_4 + 0.1\text{Na}_2\text{SO}_3$ |
| 3. $0.6\text{Na}_2\text{MoO}_4 + 0.1\text{Na}_2\text{SO}_3$ | 6. $1.2\text{Na}_2\text{MoO}_4 + 0.1\text{Na}_2\text{SO}_3$ |

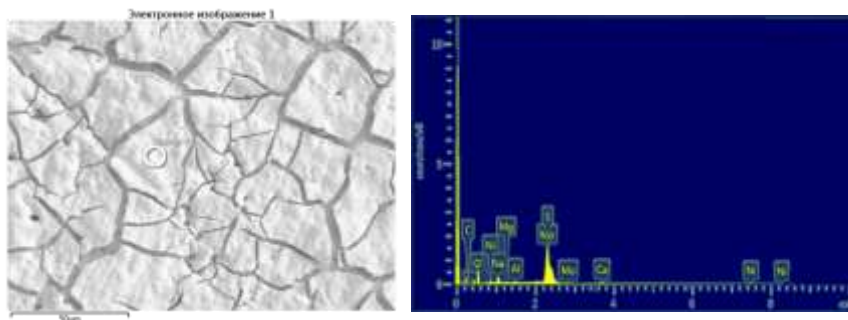


Figure 16. SEM images of electrochemically deposited Mo-S thin films.

Electrolyte (M): $1 \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + 0.1 \text{Na}_2\text{SO}_3$. T = 338K, $E_V = 0.03 \text{ V/sec}$.

The results show that thin layers with stoichiometric composition are obtained from $1.0 \text{ M Na}_2\text{MoO}_4 + 0.1 \text{ M Na}_2\text{SO}_3$ electrolyte at the current

density of 7 mA/cm^2 . In this case, the content of Mo and S in the cathode deposits is 59.8% and 40.2%, respectively. Subsequent increases in current density lead to an increase in the amount of Mo in the cathode deposits, whereas to a decrease in their quality and electrode adhesion [15].

Figure 16 shows the morphology, relief, and element composition of electrochemically deposited thin-film Mo-S samples recorded by a scanning electron microscope.

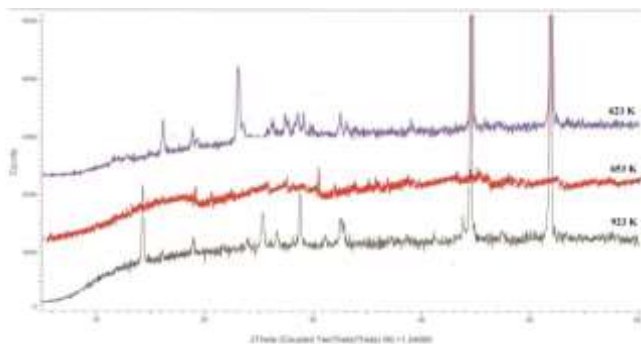


Figure 17. Results of X-ray phase analysis of electrochemically deposited thin Mo-S samples. Electrolyte (M):1 $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ + 0.1 Na_2SO_3 . $T = 338\text{K}$, $E_v=0,03 \text{ V/sec}$.

The results of the scanning electron microscope once more prove that both components are deposited together.

The electrochemical deposition of thin layers of MoS_2 was also confirmed by X-ray phase analysis (Figure 17). The figure shows 3 radiographs corresponding to the stoichiometric composition. Although the samples were deposited under the same optimal conditions, the chemical compounds with MoS_2 , Mo_3S_4 and NiMoO_4 composition were obtained at 623 K, 653 K and 923 K, respectively, depending on the heat treatment process at different temperatures in the argon atmosphere. Since the samples taken during the co-deposition process are amorphous, a heat treatment process was used to convert them into a crystalline structure.

There are 4 active modes of first-order combinatorial scattering for MoS_2 , [167, 199]: 32 cm^{-1} (E_{2g}^2), 286 cm^{-1} (E_{1g}), 383 cm^{-1} (E_{2g}^1) və 408 cm^{-1} (A_{1g}). The E_{2g}^2 mode occurs as a result of the vibration of the S - Mo - S layer relative to the adjacent layers. The E_{1g} mode refers to the vibration of a denser layer. The E_{2g}^1 plane mode occurs as a result of the

vibration of opposite direction of two S atoms to one Mo atom. The A_{1g} mode is associated with the vibration of opposite direction of only S atoms outside the plane.



Figure 18. Raman spectroscopy of electrochemically deposited thin Mo-S samples (thermally processed sample). Electrolyte (M):1 $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ + 0.1 Na_2SO_3 . Thermal processing – 623 K.

In figure 18, it seems from results of Raman spectroscopy for Mo-S samples that the active displacement of Raman radiation for molybdenum disulfide is in the range of $350\text{-}450\text{ cm}^{-1}$. That is, the above-mentioned active peaks can be seen here. In this case, the peaks at 350 cm^{-1} and 380 cm^{-1} on the surface correspond to the sulfur atoms vibrating in the same direction, and the peaks at 420 cm^{-1} correspond to the molybdenum atom.

In addition to these studies, the regression equation was calculated for Mo-S [14]:

$$\hat{y} = 40,45 + 18,425x_1 + 2.175x_2 + 17,7x_3 - 0,05x_1x_2 + 3,625x_1x_3 + 5,975x_2x_3 + 2,9x_1x_2x_3 \quad (14)$$

The obtained regression equation (14) allows calculating the amount of molybdenum in the Mo-S alloy synthesized at a given concentration of components and current density, and determining the relationship between the composition of the alloy and the parameters of electrolysis and also the composition of the electrolyte.

The photoelectrochemical properties of thin layers of semiconductor MoS_2 deposited by electrochemical methods were carried out under the influence of light and in the dark.

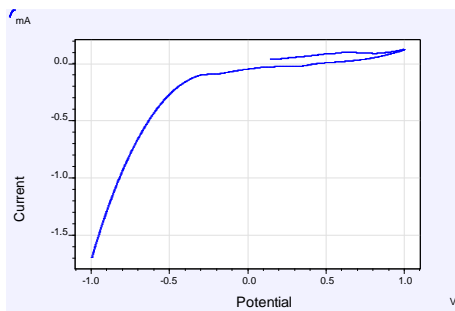


Figure 19. Polarization curve of MoS₂ sample in the dark on the ITO electrode. Electrolyte temperature T = 296K, E_v = 0.02 Vs⁻¹

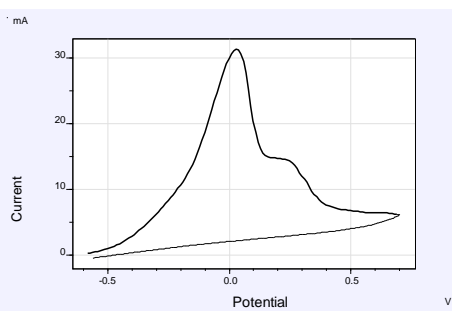


Figure 20. Polarization curve of MoS₂ sample in light on the ITO electrode. Electrolyte temperature T = 296K, E_v = 0.02 Vs⁻¹

The polarization curves of the thin layers of MoS₂ obtained on the ITO electrode in light and dark are shown in Figures 19 and 20. The experiments were implemented in a 0.5 M Na₂SO₄ solution in the potential range of 1.0- (-1.0) V.

A comparison of Figures 19 and 20 shows that the MoS₂ layer indicates photoelectrochemical properties in the polarization curve under the influence of light. This is clearly reflected in the potential range of - 0.5 - (0.5) V in the anode polarization curve. The highest result is at 0.0V potential. An increase in current towards anode indicates that the semiconductor is n-type.

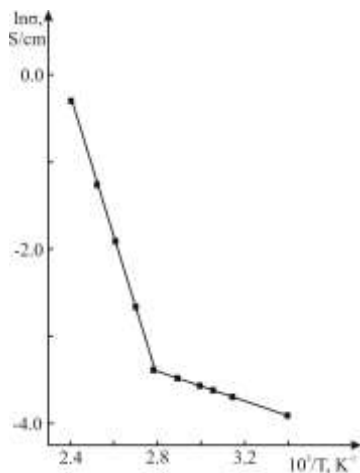


Figure 21. Temperature dependence of the specific electrical conductivity of MoS₂ semiconductor thin layers

The dependence between natural logarithm of specific electrical conductivity and temperatures, at which the resistance is measured, was plotted according to $\ln\sigma-1/T$ by measuring their resistance for MoS₂ layers.

As is seen from Figure 21, two straight lines are observed on the time-dependence curve. Here, a straight line corresponding to the temperature range 415-359 K refers to the specific conductivity of MoS₂, and a line corresponding to the temperature range 359-300 K refers to the mixed conductivity. That is, as the temperature increases, the specific conductivity of the thin layers of MoS₂ is replaced by the mixed conductivity. The values of the straight lines show that the mixed conductivity is less than the specific conductivity. This indicates that the deposited MoS₂ semiconductor layers have a small amount of additives.

It is possible to calculate the other semiconductor constants for the electrochemically deposited MoS₂ semiconductor layers by finding $\text{tg}\alpha$ separately for each of the straight lines in Figure 21. The width of forbidden band is $E_g=1.41\text{eV}$ for special conductivity, $E_g=0.19\text{ eV}$ for mixed conductivity, coefficient of sensitivity to temperature $B=16376\text{ K}$ and temperature coefficient of resistance at 300 and 415K are $\alpha^{300}=0.182\text{K}^{-1}$, $\alpha^{415}=0.095\text{K}^{-1}$. All constants for the electrochemically deposited MoS₂ semiconductor compound calculated by us are given in Table 3.

Table 3

Semiconductor constants of MoS₂ thin layers deposited from an aqueous electrolyte by electrochemical method.

Compound	ΔE_s eV	ΔE_m eV	B, K	$\alpha^{300}\text{ K}^{-1}$	$\alpha^{415}\text{ K}^{-1}$
<i>MoS₂</i>	<i>1,41</i>	<i>0,19</i>	<i>16376</i>	<i>1.82×10⁻¹</i>	<i>9.5×10⁻²</i>

As a follow-up of the study, it was confirmed that the thin layers of the MoS₂ semiconductor have an "n" -type conductivity by the thermozoning method.

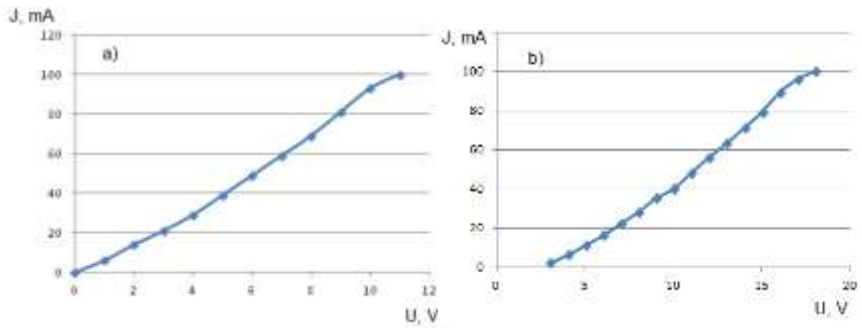


Figure 22. The study of volt-ampere characteristic of MoS₂ sample in tablet form. a) Thermally processed sample; b) non-heat treated sample

Volt-ampere characteristics of MoS₂ thin films have also been studied. Analytically, this effect is given in the form of a graphical relationship between electric current and corresponding voltage. Using this graph, it is possible to analyze the electrical properties of semiconductors.

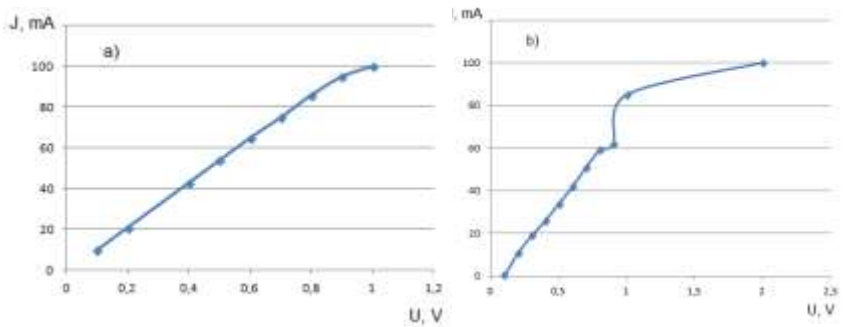


Figure 23. Investigation of volt-ampere characteristics for MoS₂ sample in the form of thin layer. a) Thermally processed sample; b) non-heat treated sample

As can be seen from Figures 22 and 23, the study of the volt-ampere characteristics for the MoS₂ sample was accomplished with both tablet and thin-film samples. The graphical view of the tablet-shaped sample shows that the value of the current starts from zero and increases in proportion to the electric field. This shows that in this MoS₂ sample, the Fermi level is centered and the difference between the electrons and the

density of the holes is small. For this reason, there is no sharp change in the graph (Figure 22 a and b).

A graphical view of the volt-ampere characteristic of MoS₂ sample in the form of thin-layer (Figure 23. a) shows that at first, the characteristic rises sharply unlike massive semiconductors, and then saturation occurs for some time. In this part, the density of the holes becomes equal to the electrons. At a certain value of the electric field – in the range of about 0.8-1.0 V, the value of the current increases. As the electric field increases, the flow of charge carriers from the inside of the crystal to its surface increases also and stops when they reach the surface. Since the thin layer is in contact with the air layer, the rate of recombination prevails over the rate of generation, so an infinite straight line is observed. It should also be noted that the presence of this straight line in the volt-ampere characteristic plays a key role in the design of devices and is called "working zone". This stability of the characteristic is very important, especially in device fabrication. As can be seen in Figure 23 b, a sharp change is observed. This change is most likely due to nanostructures formed during the technological process on the surface. As is well known, tunnel junction is an event in semiconductors explained by the laws of quantum physics. Therefore, the anomaly observed in Figure 23 b is not explained by the displacement at the Fermi level, that by a sharp change in the properties of the nanostructures due to external influences. This is also observed during the measuring the photoconductivity of the layer (Figure 24).

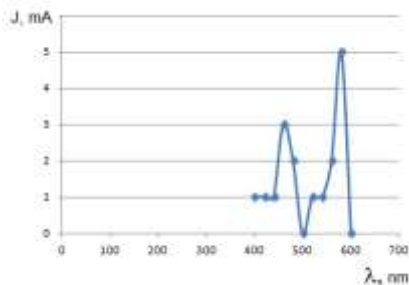


Figure 24. Measurement of photoconductivity of a thin MoS₂ layer

The intensive change of current around the wavelength of $\lambda= 500\text{-}580\text{nm}$ considerably changes the physical properties of nanostructures

due to the red wave with high energy. This can also occur due to the increase in concentration of additives.

The thickness of the thin layers obtained as a result of electrochemical deposition is 4-6 μk . This satisfies their demand for photovoltaic materials in solar cells [16].

All these constants calculated for thin layers of MoS_2 semiconductor are considered to be basic factors in their future application. Because, without knowing properties of semiconductor layers, it may create certain difficulties for employees working in this field to determine the applications of synthesized ones. All calculated constants of the MoS_2 compound synthesized by us open up wide possibilities for the application of this compound in electronics.

CONCLUSION

1. Joint electrochemical deposition of molybdenum and sulfur from an aqueous electrolyte was carried out. The nature of polarization was studied for the process of separate electroreduction of molybdenum and sulfur in the study. It was found that the deposition of molybdenum from the aqueous electrolyte, on the platinum electrode, in the potential range of 0.47 - (-0.8) V, takes place in stages, the nature of the polarization is first electrochemical and then accompanied by the concentration polarization. The electroreduction processes of sulfite and thiosulfate ions from the aqueous electrolyte have been studied on platinum and molybdenum electrodes, respectively. This process occurs on the Pt electrode in the potential range of 0.4–(-0.7) V, and on the Mo electrode in the potential range of 0.1–(-1.0) V. The kinetics of the reduction process is accompanied by electrochemical polarization.
2. The process of electrolytic codeposition of aqueous solution of molybdenum and sulfur on different electrodes (Pt and Ni) was studied by recording cyclic and cathode polarization curves. It was found that, depending on the material of the electrode, along with the change in the rate of the electrochemical reaction, the potential field of codeposition also differs significantly. Thus, while the co-deposition process of molybdenum and sulfur on platinum electrodes takes place at a potential of -0.5 - (-0.65) V, on the Ni electrode this process occurs at a potential of -0.55 - (-1.0) V.
3. The influence of various factors (current density, temperature, total concentration, concentration of the components, etc.) on the

composition of thin Mo - S layers deposited from an aqueous solution by electrochemical way was studied. The electrolyte composition was determined for the electrochemical deposition of thin semiconductor layers corresponding to the stoichiometric composition (MoS_2) from the aqueous solution, and the electrolysis condition were selected as a result of the researches. The following electrolyte composition and electrolysis condition were proposed (mol/L): 1.0M Na_2MoO_4 +0.1M Na_2SO_3 , current density $i_k = 7\text{A}/\text{dm}^2$, $T=338\text{K}$. Anode - platinum, cathode - platinum, nickel.

4. The regression equation was created for the process of electrochemical obtaining the molybdenum-sulfur thin layers from molybdate and sulfite electrolytes by the method of statistical design of experiments. This equation relates the amount of components in the thin layers to the electrolyte composition and the electrolysis conditions.
5. The morphology, chemical composition and structure of molybdenum-sulfur thin layers obtained by electrochemical methods were studied by scanning electron microscopic, X-ray phase and Raman spectroscopy methods. As a result of the research, it was found that the fine crystalline chemical compound with composition of Mo_3S_4 are formed along with MoS_2 by the electrolytic deposition of the aqueous solution on the surface of the cathode.
6. The semiconductor properties of electrochemically obtained Mo-S thin films were studied and it was determined that they have an “n” type conductivity. The temperature dependence of the electrical conductivity of the obtained layers and some semiconductor constants were determined (thermal sensitivity coefficient - B, activation energy of electrical conductivity - ΔE , forbidden energy band, etc.). The obtained values show that the low value of electrical resistance and temperature coefficient of thin layers of chemical compound MoS_2 obtained by electrolysis allows these compounds to be used in electronics.
7. Photoelectrochemical properties of electrochemically synthesized Mo-S thin layers were studied. According to the chronoamperometric and chronopotensimetric curves, MoS_2 is n-type as well as photosensitive semiconductor compound. In this respect, electrochemically deposited MoS_2 thin layers can be used as one of the components in photoelectronics and in new-generation solar cells.

The main results of the dissertation have been published in the following scientific works:

1. Алиев А.Ш., Джафарова С.Ф., Солтанова Н.Ш. Исмаилов Д.Г. Электрохимическое получение тонких полупроводниковых пленок MoS_2 для преобразования солнечной энергии / Альтернативные источники сырья и топлива, тезисы докладов V международной научно-технической конференции г. Минск, Беларусь, 2015, 26-28 мая, с. 71.
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The defense will be held on 29 june 2021 at 10⁰⁰ at the meeting of the Dissertation council BED 1.15 on specialties 2308.01 - "Electrochemistry" and 2303.01 - "Inorganic Chemistry" established on the basis of ED 1.15 Dissertation Council of the Supreme Attestation Commission under the President of the Republic of Azerbaijan under the Institute of Catalysis and Inorganic Chemistry named after M. Nagiyev of ANAS

Address: Baku city, H. Javid Avenue, 113

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Abstract was sent to the required addresses on 25 may 2021.

Signed for print: 08.05.2021

Paper format: A5

Volume: 39690

Number of hard copies: 20