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ҚАЙЫРЫМДЫЛЫҚ ҚОРЫ
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«ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ» РҚБ
«ХАЛЫҚ» ЖҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

РОО «НАЦИОНАЛЬНОЙ
АКАДЕМИИ НАУК РЕСПУБЛИКИ
КАЗАХСТАН»
ЧФ «Халык»

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В 2016 году для развития и улучшения качества жизни казахстанцев был создан частный Благотворительный фонд «Халык». За годы своей деятельности на реализацию благотворительных проектов в областях образования и науки, социальной защиты, культуры, здравоохранения и спорта, Фонд выделил более 45 миллиардов тенге.

Особое внимание Благотворительный фонд «Халык» уделяет образовательным программам, считая это направление одним из ключевых в своей деятельности. Оказывая поддержку отечественному образованию, Фонд вносит свой посильный вклад в развитие качественного образования в Казахстане. Тем самым способствуя росту числа людей, способных менять жизнь в стране к лучшему – профессионалов в различных сферах, потенциальных лидеров и «великих умов». Одной из значимых инициатив фонда «Халык» в образовательной сфере стал проект Ozgeris powered by Halyk Fund – первый в стране бизнес-инкубатор для учащихся 9-11 классов, который помогает развивать необходимые в современном мире предпринимательские навыки. Так, на содействие малому бизнесу школьников было выделено более 200 грантов. Для поддержки талантливых и мотивированных детей Фонд неоднократно выделял гранты на обучение в Международной школе «Мирас» и в Astana IT University, а также помог казахстанским школьникам принять участие в престижном конкурсе «USTEM Robotics» в США. Авторские работы в рамках проекта «Тәлімгер», которому Фонд оказал поддержку, легли в основу учебной программы, учебников и учебно-методических книг по предмету «Основы предпринимательства и бизнеса», преподаваемого в 10-11 классах казахстанских школ и колледжей.

Помимо помощи школьникам, учащимся колледжей и студентам Фонд считает важным внести свой вклад в повышение квалификации педагогов, совершенствование их знаний и навыков, поскольку именно они являются проводниками знаний будущих поколений казахстанцев. При поддержке Фонда «Халык» в южной столице был организован ежегодный городской конкурс педагогов «Almaty Digital Ustaz.

Важной инициативой стал реализуемый проект по обучению основам финансовой грамотности преподавателей из восьми областей Казахстана, что должно оказать существенное влияние на воспитание финансовой грамотности и предпринимательского мышления у нового поколения граждан страны.

Необходимую помощь Фонд «Халык» оказывает и тем, кто особенно остро в ней нуждается. В рамках социальной защиты населения активно проводится

работа по поддержке детей, оставшихся без родителей, детей и взрослых из социально уязвимых слоев населения, людей с ограниченными возможностями, а также обеспечению нуждающихся социальным жильем, строительству социально важных объектов, таких как детские сады, детские площадки и физкультурно-оздоровительные комплексы.

В копилку добрых дел Фонда «Халык» можно добавить оказание помощи детскому спорту, куда относится поддержка в развитии детского футбола и карате в нашей стране. Жизненно важную помощь Благотворительный фонд «Халык» оказал нашим соотечественникам во время недавней пандемии COVID-19. Тогда, в разгар тяжелой борьбы с коронавирусной инфекцией Фонд выделил свыше 11 миллиардов тенге на приобретение необходимого медицинского оборудования и дорогостоящих медицинских препаратов, автомобилей скорой медицинской помощи и средств защиты, адресную материальную помощь социально уязвимым слоям населения и денежные выплаты медицинским работникам.

В 2023 году наряду с другими проектами, нацеленными на повышение благосостояния казахстанских граждан Фонд решил уделить особое внимание науке, поскольку она является частью общественной культуры, а уровень ее развития определяет уровень развития государства.

Поддержка Фондом выпуска журналов Национальной Академии наук Республики Казахстан, которые входят в международные фонды Scopus и Wos и в которых публикуются статьи отечественных ученых, докторантов и магистрантов, а также научных сотрудников высших учебных заведений и научно-исследовательских институтов нашей страны является не менее значимым вкладом Фонда в развитие казахстанского общества.

С уважением,
Благотворительный Фонд «Халык»!

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ELECTROCHEMICAL DEPOSITION OF BISMUTH SULFIDE THIN FILMS

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Abstract. An urgent task is the development of methods for the synthesis of compounds of metals and semiconductors with mixed anions (for example, chalcohalides or sulfur halides) with an advanced morphology, capable of absorbing a wide range of solar radiation. An important task is the fabrication of photoelectrodes for the

implementation of photoelectrochemical, photocatalytic reactions in liquid media (PEC cells). This paper describes the effect of the electrolyte solution, the concentration of the initial reagents and the substrate material on the electrochemical behavior of bismuth and sulfur ions. Cyclic voltammetry, XRD, SEM, photoelectrochemical measurements were used for characterization. The optimal conditions for the electrochemical synthesis of bismuth sulfide thin films are determined. The surface morphology and composition of Bi_2S_3 were dependent on the synthesis potentials. Bi_2S_3 thin films, obtained at E= -750 mV, possessed a continuous surface and high crystallinity, and demonstrate the photocurrent density 22 μA/cm^2 in 0.5 M Na_2SO_4 under AM1.5G illumination. The achieved photoelectrochemical characteristics prove the applicability of the synthesized bismuth sulfide thin films in photoelectrochemical devices.

Keywords: thin films, bismuth semiconductor compounds, bismuth sulfide, electrodeposition

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ВИСМУТ СУЛЬФИДІНІҢ ЖҰҚА ҚАБЫРШАҒЫНЫҢ ЭЛЕКТРОХИМИЯЛЫҚ ТҰНДЫРУЫ

Аннотация. Күн радиациясының кең спектрін сіңіруге қабілетті морфологиясы дамыған аралас аниондармен (мысалы, халкогалидтер немесе күкіртгалогенидтері) металдар мен жартылай өткізгіштердің қосылыстарын синтездеу әдістерін әзірлеу өзекті мәселе болып табылады. Сондай-ақ сұйық ортада фотоэлектрохимиялық, фотокаталитикалық реакцияларды жүзеге асыру үшін фотоэлектродтарды жасау маңызды міндет болып табылады (PEC жасушалар). Бұл мақалада электролит ерітіндісінің, бастапқы реагенттер концентрациясының және төсеніш материалының висмут пен күкірт иондарының электрохимиялық әрекетіне әсері сипатталған. Сипаттама үшін циклдік вольтаметрия, РФА, SEM және фотоэлектрохимиялық өлшемдер қолданылды. Висмут сульфидінің жұқа қабықшаларының электрохимиялық синтезінің оңтайлы шарттары анықталды. Bi_2S_3 бетінің морфологиясы мен құрамы синтез потенциалдарына байланысты болды. E= -750 мВ кезінде алынған Bi_2S_3 жұқа қабықшалары үздіксіз бетке және жоғары кристалдылыққа ие болды, AM 1,5G жарықтандыру кезінде 0,5

М Na_2SO_4 ішінде 22 мкА/см^2 фототок тығыздығын көрсетті. Қол жеткізілген фотоэлектрохимиялық сипаттамалар висмут сульфидінің синтезделген жұқа қабықшаларының фотоэлектрохимиялық құрылғыларда қолданылуын дәлелдейді.

Түйін сөздер: жұқа қабықшалар, висмут жартылай өткізгіш қосылыстары, висмут сульфиді, электротұндыру

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ЭЛЕКТРОХИМИЧЕСКОЕ ОСАЖДЕНИЕ ТОНКИХ ПЛЕНОК СУЛЬФИДА ВИСМУТА

Аннотация. Актуальной задачей является разработка методик синтеза соединений металлов и полупроводников со смешанными анионами (например, халькогалогениды или галогениды серы) с развитой морфологией, способных сорбировать широкий диапазон солнечного излучения. Важной задачей также является изготовление фотоэлектродов для осуществления фотоэлектрохимических, фотокаталитических реакций в жидких средах (PEC ячейки). В данной статье описано влияние раствора электролита, концентрации исходных реагентов и материала подложки на электрохимическое поведение ионов висмута и серы. Для характеризации использовались циклическая вольтамперометрия, рентгенография, СЭМ, фотоэлектрохимические измерения. Определены оптимальные условия для электрохимического синтеза тонких пленок сульфида висмута. Морфология поверхности и состав Bi_2S_3 зависели от потенциалов синтеза. Тонкие пленки Bi_2S_3, полученные при E= -750 мВ, обладали сплошной поверхностью и высокой кристалличностью, демонстрировали плотность фототока 22 мкА/см^2 в 0,5 М Na_2SO_4 при освещении AM 1,5G. Достигнутые фотоэлектрохимические характеристики доказывают применимость синтезированных тонких пленок сульфида висмута в фотоэлектрохимических устройствах.

Ключевые слова: тонкие пленки, полупроводниковое соединение висмута, сульфид висмута, электроосаждение

Introduction

One of the most urgent tasks of modern science is the development of methods and devices for converting of solar radiation into thermal and electrical energy. Various thermal systems, solar collectors and concentrators are used to generate heat energy. The ability of some semiconductor compounds and their combinations with nonmetals/

metals convert the energy of absorbed photons into electricity is used to generate electricity.

Among the wide variety of semiconductor materials investigated for use in solar cells and photoelectrochemical cells (PEC cells), bismuth compounds attract attention because they are non-toxic, cheap to produce, and capable of absorbing most of the visible spectrum. Bismuth compounds, due to its qualities, are used in various photovoltaic and energy storage devices (Devi & Ray, 2020; Sun et al., 2015), in the manufacture of photocatalytic materials (Xu et al., 2019), gas sensors, in systems for photocatalytic decomposition of organic pollutants and phenol red, in X-ray and γ-ray detection systems (Frutos, 2017).

Bismuth double chalcogenides (Bi_2X_3, where X = S, Se, Te) are characterized by high stability, photosensitivity, and thermoelectric properties (Riahi et al., 2017). Bismuth sulfide, is n-type semiconductor with a plate structure, the band gap lies in the range between 1.5 and 1.9 eV (Gao et al., 2011). Bi_2S_3 is characterized by electrical conductivity about 10^{-6}– 10^{-7} $\Omega^{-1}cm^{-1}$ and a high radiation absorption coefficient $\alpha > 10^5$ cm^{-1} in the visible region (Cruz-Gómez et al., 2022), which makes it possible to consider this compound a promising material for use in optoelectronic, photovoltaic and photoelectrochemical devices, and also as anodes for all-solid-state lithium-ion batteries (Kumari et al., 2019). In addition to its utilization in various photoelectrochemical devices, this compound has found application in systems for the photocatalytic reduction of CO_2 and Cr(IV) (Jin & He, 2017; Luo et al., 2017).

Bi_2S_3 crystallizes in the orthorhombic space group Pnma with lattice parameters a = 4.025, b = 11.170, c = 11.735 Å, z = 4 (Fig. 1.) (Jain et al., 2013). The structure is three-dimensional, with 4 molecules per unit cell (Persson, 2014).

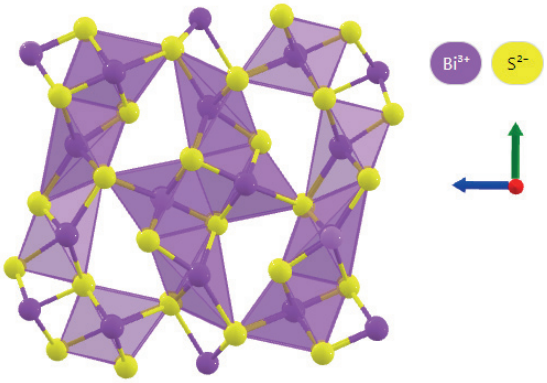


*Fig. 1.*Structure of bismuth sulfide Bi_2S_3 (Jain et al., 2013)

Bismuth sulfide thin films are obtained by various methods, such as spray pyrolysis (Medles et al., 2006), chemical bath deposition (Moreno-García et al., 2014), solvothermal synthesis (Jin & He, 2017), vacuum thermal evaporation (Ten Haaf et al., 2013). The disadvantages of these methods are the use of complex equipment, the process duration, the need to use high temperatures.

For the synthesis of semiconductor thin-film coatings, electrochemical methods are popular and actively studied. Such methods are distinguished by the process simplicity, the cheapness of the equipment, the possibility of controlling the surface morphology and the composition of the resulting films by varying the deposition conditions, the possibility of modifying the films surface. The advantage of electrochemical processes is the possibility of obtaining thin films at room temperature on substrates of any area.

Among the electrochemical methods for Bi_2S_3 thin films synthesis, the most commonly used method is cathodic electrodeposition onto ITO/glass substrates (glass/indium tin oxide) (Yan Wang et al., 2009), FTO/glass (glass/fluorinated tin oxide) (Shinde et al., 2009), or carbon fiber (Jagadish et al., 2016). New methods are also being developed, for example, rectangular voltammetry method (Chahkandi & Zargazi, 2019), ultrasonic cathode electrodeposition (Y. Wang et al., 2011). A significant disadvantage of these works is the lack of detailed studies on the electrochemical behavior of Bi^{3+} and S^{2-} ions in various electrolytes, as well as the effect of the initial reagents ratio on the type of I-V curves.

The aim of this work is to study the influence of the substrate material, the composition of electrolytes and the concentration of initial reagents on the voltage dependences and the process of electrochemical deposition of Bi_2S_3 thin films.

Materials and methods

The study of the electrochemical behavior of Bi^{3+} and S^{2-} ions in different electrolyte solutions was carried out in a standard three-electrode cell at room temperature. A glass-carbon disk electrode (S = 0.07 cm^2) and an electrode made of glass coated with conductive fluorinated tin oxide (FTO/glass) with an area of 1.5–2.0 cm^2 were used as working electrodes to obtain current-voltage curves. A platinum spiral with a surface area ≈1.5 cm^2 was used as a counter electrode. A silver chloride electrode (Ag/AgCl) in a 3 M KCl solution was used as a reference electrode. All experimentally obtained potential values are given relative to the silver chloride reference electrode. AP-45X potentiostat-galvanostat (Electrochemical Instruments) was used to obtain current-voltage dependences and electrodeposition of bismuth sulfide thin films.

$Bi(NO_3)_3 \cdot 5H_2O$ (c.p.) were used to prepare electrolytes. Three electrolyte solutions were studied - based on nitric acid, EDTA-Na and water. To prepare the first electrolyte, bismuth nitrate was dissolved in 10% HNO_3, pH = 1. The use of nitric acid as an electrolyte during the electrodeposition of Bi_2S_3 is complicated by the fact that Bi(III) bismuth salts in strongly acidic solutions (pH>1.8) undergo hydrolysis (pK_g = 1.58) with the formation of both single-core particles $[BiOH]^{2+}$, $[Bi(OH)_2]^{+}$, and more complex particles of cluster type (Petrova, 2012). Therefore, the second electrolyte was prepared by dissolving bismuth nitrate in $9 \cdot 10^{-3}$M EDTA-Na at room temperature. An electrolyte with pH = 4 was obtained. The third electrolyte was distilled water, where bismuth nitrate was dissolved using ultrasonic stirring. A solution of sodium thiosulfate $Na_2S_2O_3$ was used as a source of sulfur ions.

Electrochemical deposition of Bi_2S_3 was carried out on FTO/glass from electrolyte with EDTA-Na, $3 \cdot 10^{-3}$ M $Bi(NO_3)_3 \cdot 5H_2O$ and $6 \cdot 10^{-3}$M $Na_2S_2O_3$, (pH=4), during 30 minutes, with stirring of the electrolyte. The electrodeposition potential was varied from -525 mV to -750 mV to study its effect on the morphology and composition of bismuth sulfide thin films.

Before electrodeposition, the FTO/glass substrates were washed with ethanol, soap solution, distilled water. Then the substrates were boiled for 10 minutes in a solution of 0.8 M H_2O_2 + 0.6 M NH_4OH. After boiling, the substrates were repeatedly washed with distilled water and dried in an air stream.

The morphology of Bi_2S_3 films was determined using an electron microscope JSM 6610 LV (JEOL). The phase composition of electrodeposited films was analyzed using a DRON-4-07 diffractometer in the 25 kV, 25 mA mode, using a tube with a cobalt anode. The parameters of the crystal lattice were determined by comparing experimental calculated data with known reference data.

Photoelectrochemical measurements were carried out in an aqueous solution 0.5 M Na_2SO_4 at 25 °C using GillAC potentiostat-galvanostat (ACM Instruments). A Xenon Solar simulator XSS-5XD with a 500 W xenon lamp (AM1.5G) was used to generate chopped illumination for PEC study. The light power density was 100 mW/cm^2. The determination of the photopotential was carried out by measuring the open circuit potential E_{OC}, without applying an external voltage, when the electrode was illuminated in a solution of 0.5 M Na_2SO_4.

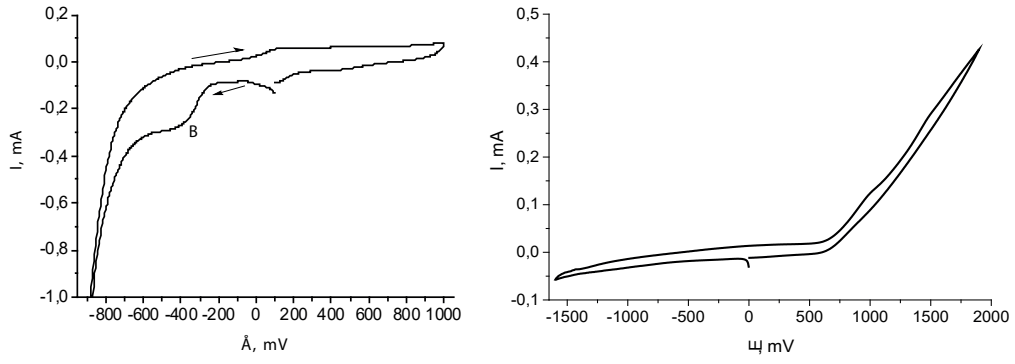
Results and discussion

Analysis of current-voltage curves

The study of the electrochemical behavior of Bi(III) and S(II) ions was carried out on a glass-carbon electrode at different concentrations of bismuth and sulfur ions in electrolytes with different pH.

In order to study the effect of the supporting electrolyte composition on the reduction and oxidation of Bi(III) ions, I-V curves were obtained. An aqueous acidic electrolyte based on 10% HNO_3 and an electrolyte with additives of $9 \cdot 10^{-3}$ M EDTA-Na complexing agent was investigated at different concentrations of bismuth ions, at a potential sweep rate 20 mV/s.

The current-voltage curves of supporting electrolytes without addition Bi(III) and S(II) ions are demonstrated in Fig. 2.

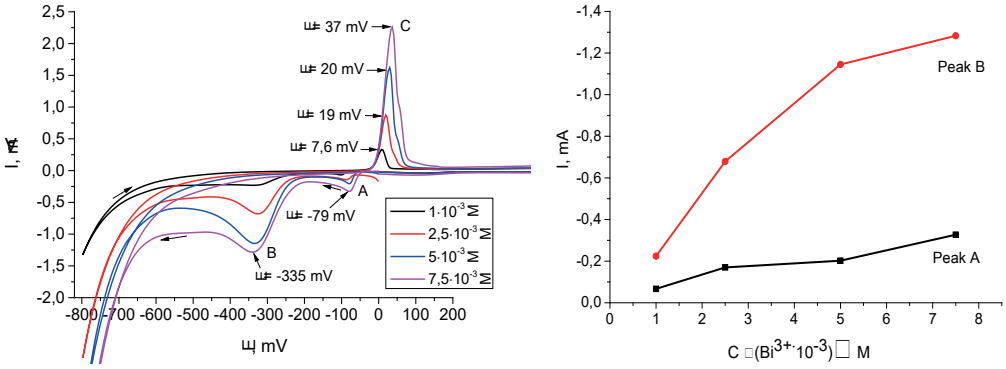


a b

Fig. 2. Current-voltage curves of supporting electrolytes:
a) 10% HNO_3; b) $5 \cdot 10^{-3}$ M EDTA-Na

A small reduction peak is observed at E = -345 mV in the cathode area on the I-V curve of 10 % HNO_3 (Fig. 2, a.). During scanning the potential to the anode region, no oxidative processes are observed. In EDTA-Na electrolyte (Fig. 2, b), a significant increase in the anode current is observed at high positive potentials (E = 750 mV). During scanning the potential into the cathode region, no reduction processes are observed.

The effect of bismuth ions concentration on the I-V curves at 10% HNO_3 is investigated (Fig. 3.).



a b

*Fig. 3.*a)I-V curves of Bi(III) ions in 10% HNO_3; b) the dependence of the reduction current peaks on the concentration of bismuth ions in the solution

In the nitric acid electrolyte, the Bi(III) I-V curve has two reduction peaks at E = -79 mV (peak A) and E = -335 mV (peak B) in the cathode area and one oxidation peak at E = 7.6 ~ 37 mV in the anode area (fig. 3, a). At the potential E = -78 ~ 80 mV (the first reduction peak A), two reactions can occur - the deposition of bismuth on the electrode at undervoltage or the reduction of nitrate ions according to reactions (1 and 2) (Bilican et al., 2017; Petrova, T.P., Shapnik, A.M., Rakhmatullina, 2012):

$$NO^{3-} + 2H_2O + 3e^- = NO(g) + 4OH^-,\ E^0 = -0.14\ V(SHE) \quad (1)$$

$$NO^{3-} + H_2O + 2e^- = NO^{2-} + 2OH^-,\ E^0 = 0.01\ V\ (SHE) \quad (2)$$

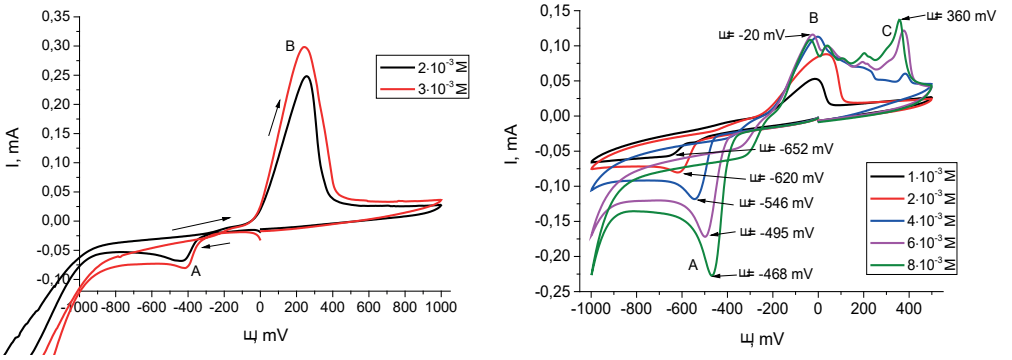
At a potential E = – 335 mV, Bi(III) ions are reduced via reaction (3):

$$Bi^{3+} + 3e^- = Bi^0 \quad (3)$$

With an increase in the concentration of bismuth nitrate, there is a sharp increase in the reduction currents (peak B) and oxidation currents (Fig. 3, a.). The dependence of the Bi(III) ions reduction currents on their concentration in the electrolyte is shows, that the value of the peak A current slightly depends on the concentration of Bi(III) ions (Fig. 3, b.). This confirms the assumption that this peak refers to the reduction of nitrate ions. On the contrary, peak B currents increase in proportion to the concentration of Bi(III)

ions. With an increase the amount of deposited bismuth on the electrode, a slight shift in the potentials of its oxidation peaks is observed in the anodic scan.

In order to confirm that the reduction of nitrate ions occurs on a glassy carbon electrode in a nitric acid electrolyte at potentials E = -78 ~ 80 mV (Fig. 3, a.), the electrochemical reduction and oxidation of bismuth ions in water and in an aqueous electrolyte with the addition of the EDTA-Na complexing agent (Fig. 4, a, b.). The dissolution of bismuth nitrate in water was carried out in an ultrasonic bath.



a b

Fig. 4. I-V curves of $Bi(NO_3)_3 \cdot 5H_2O$ reduction-oxidation in: a) aqueous electrolyte; b)$9 \cdot 10^{-3}$ M EDTA-Na electrolyte

Analysis of the I-V curves of bismuth ions determined in two different electrolytes showed the presence of one reduction peak (peak A), at E = -400 mV in aqueous solution (Fig. 4, a.) and at E = -468 ~ -652 mV, in EDTA-Na electrolyte (Fig. 4, b.). In this case, the reduction of Bi(III) ions shifts towards negative potentials. In both electrolytes, a shift in the reduction peak potential to the positive region is observed with an increase in the concentration of bismuth nitrate (Fig. 4, a, b.). In the two studied solutions, no reduction peaks are observed at potentials E = -78 ~ 80 mV, which may indicate that reactions (1 and 2) of nitrate reduction proceed in a nitric acid solution at this potential. The oxidation peaks are different for bismuth deposits obtained by reduction on a glassy carbon electrode from various electrolytes. In the first electrolyte, one oxidation peak (peak B) is observed at E = 245 ~ 255 mV (Fig. 3, a.). In the EDTA-Na electrolyte, two oxidation peaks are observed at potential E = -20 mV (peak B) and at E = 350 ~ 360 mV (peak C) (Fig. 3, b.). There is an increase in oxidation currents with an increase of bismuth concentration from $1 \cdot 10^{-3}$ to $8 \cdot 10^{-3}$ M. The appearance of these peaks is associated with the formation of bismuth complexes with EDTA-Na in solution.

The joint reduction of Bi(III) and S(II) ions on a glassy carbon electrode in order to determine the Bi_2S_3 electrodeposition potential was studied by recording the current-voltage curves in $9 \cdot 10^{-3}$ M EDTA-Na electrolyte (Fig. 5.).

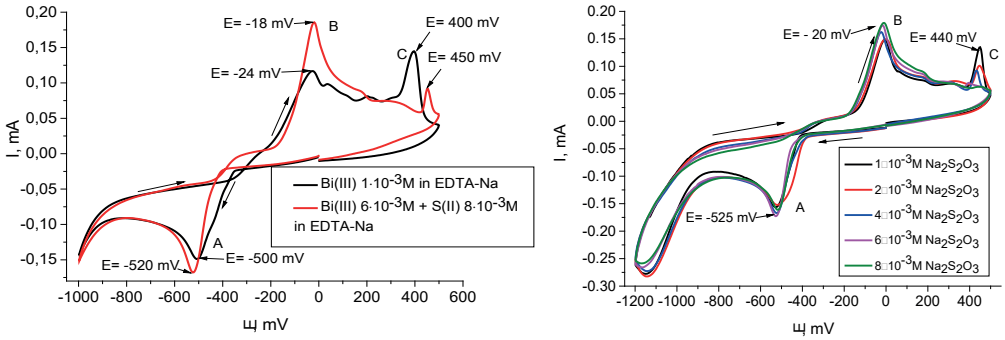


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Fig. 5. I-V curves of reduction-oxidation:
a) $6 \cdot 10^{-3}$ M $Bi(NO_3)_3 \cdot 5H_2O$ and $6 \cdot 10^{-3}$ M $Bi(NO_3)_3 \cdot 5H_2O$ + $8 \cdot 10^{-3}$ M $Na_2S_2O_3$;
b) $6 \cdot 10^{-3}$ M $Bi(NO_3)_3 \cdot 5H_2O$ + various concentrations of $Na_2S_2O_3$ in $9 \cdot 10^{-3}$M EDTA-Na

On the current-voltage curves of joint reduction-oxidation of $6 \cdot 10^{-3}$ M $Bi(NO_3)_3 \cdot 5H_2O$ + $8 \cdot 10^{-3}$ M $Na_2S_2O_3$ in $9 \cdot 10^{-3}$ M EDTA-Na, a shift of the reduction peak B to the negative region by 20 mV is observed (Fig. 5, a.). The potentials of the oxidation peaks shifted to the positive region. This is due to the formation of the Bi_2S_3 compound during the deposition according to reaction 4:

$$2Bi^{3+} + 3S^{2-} = Bi_2S_3 \qquad (4)$$

Oxidation of this compound from the electrode surface is accompanied by the appearance of a characteristic oxidation current peak C at E= -450 mV. An increase in the concentration of S(II) ions in the electrolyte from $1 \cdot 10^{-3}$ to $8 \cdot 10^{-3}$ M $Na_2S_2O_3$ affects the form of current-voltage curves (Fig. 5, b.). Thus, it can be expected, the more negative potentials than -520 mV are the most suitable for electrodeposition of bismuth sulfide in the potentiostatic mode on a glass-carbon electrode.

Since the electrodeposition of bismuth sulfide for photovoltaic applications was performed on FTO substrate, the current-voltage curves of the joint reduction-oxidation of Bi(III) and S(II) in $9 \cdot 10^{-3}$ M EDTA-Na were also studied (Fig. 6.).

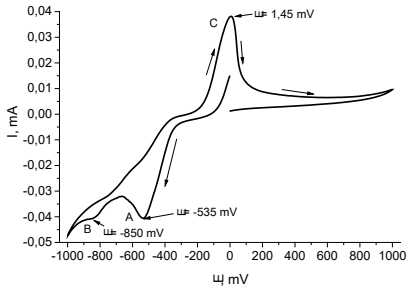

Fig. 6. I-V curves of joint reduction-oxidation of $3 \cdot 10^{-3}$ M $Bi(NO_3)_3 \cdot 5H_2O$ and $5 \cdot 10^{-3}$ M $Na_2S_2O_3$ in $9 \cdot 10^{-3}$M EDTA-Na on FTO/glass

There is one clear reduction peak (peak A) at E = -535 mV, in the I-V curve obtained on the FTO/glass electrode, which is close to the potential of peak A obtained on a glass-carbon electrode (Fig. 6.). There is also a weak reduction peak B at E= -850 mV, which may be associated with the joint deposition of Bi and S. A similar assumption was made in (Riahi et al., 2017), where the authors observed a clear reduction peak at E= -950 mV relative to SCE (E= -906 mV vs. Ag/AgCl) on an ITO substrate in a solution of 6.250 mM $Bi(NO_3)_3 \cdot 5H_2O$, 9.375 mM EDTA-Na, and 1.875 mM $Na_2S_2O_3$. At the same time, the oxidation peak C of the deposited product is much more negative and equals E = 1.45 mV. To confirm the composition of the thin film, formed on the FTO/glass electrode, further X-ray studies were performed.

Electrodeposition of Bi_2S_3 films

Based on the above study, the deposition of Bi_2S_3 films on FTO/glass was carried out in an electrolyte (pH=4) with the addition of EDTA-Na as a complexing agent at potentials E= -520, -535, -750 mV, during 30 min.

The resulting films are gray for deposition potentials E= -520, -535 mV and dark gray for potential E= -750 mV. Since the color of elemental Bi is silver gray, and Bi_2S_3 is black-brown, it can be assumed that at less negative potentials (E = -520, -535 mV) Bi is reduced according to reaction 3, and the formation of Bi_2S_3according to reaction 4 is minimal, since Bi is bound into a complex compound with EDTA-Na. This assumption is confirmed by studies of the of freshly deposited film's structure (Fig. 7, spectra a and b.). At more negative potential (E = -750 mV), the deposited films color becomes dark gray, which indicates the formation of the Bi_2S_3 compound, and is confirmed by the results of the XRD (Fig. 7, spectra c and d.).

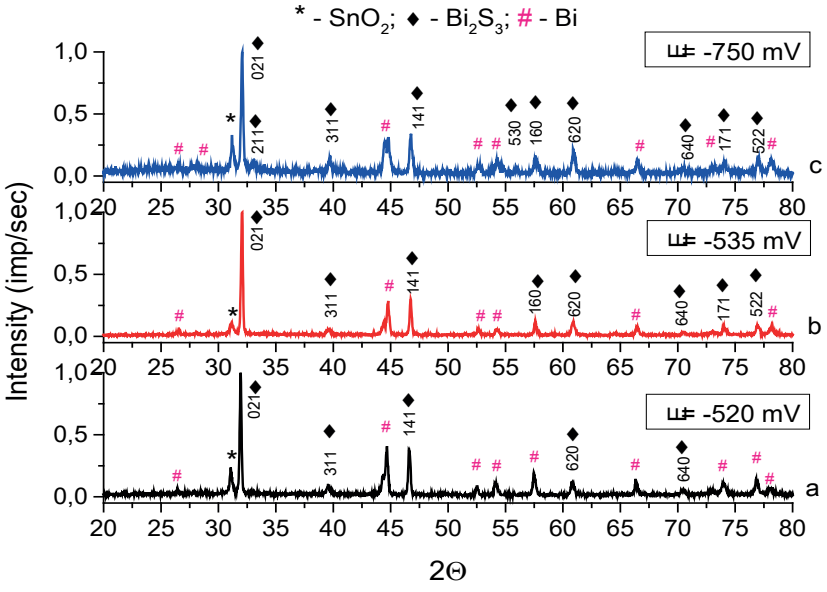

Fig. 7. XRD spectra of films deposited at a potential of: a) E = -520 mV; b) E= -535 mV; c) E= -750 mV

According to the XRD (Fig. 7.), the presence of the Bi_2S_3 compound is confirmed in the deposited films, there are also reflections characteristic of Bi and reflections of the FTO/glass (SnO_2) substrate. As the electrodeposition potential increases, the number and intensity of Bi_2S_3 signals increase. The compound crystallizes in an orthorhombic space group. The most intense reflections observed at the crystallographic directions (021), (311), (620), (171), (262), which corresponds to the ASTM tabular data (JCPDS 170320) for the Bi_2S_3 compound. The low intensity of the SnO_2 substrate reflections relative to the reflections of Bi_2S_3 indicates about a uniform coverage of the substrate surface with the Bi_2S_3 film. This assumption confirmed by the data of scanning electron microscopy (Fig. 8.).

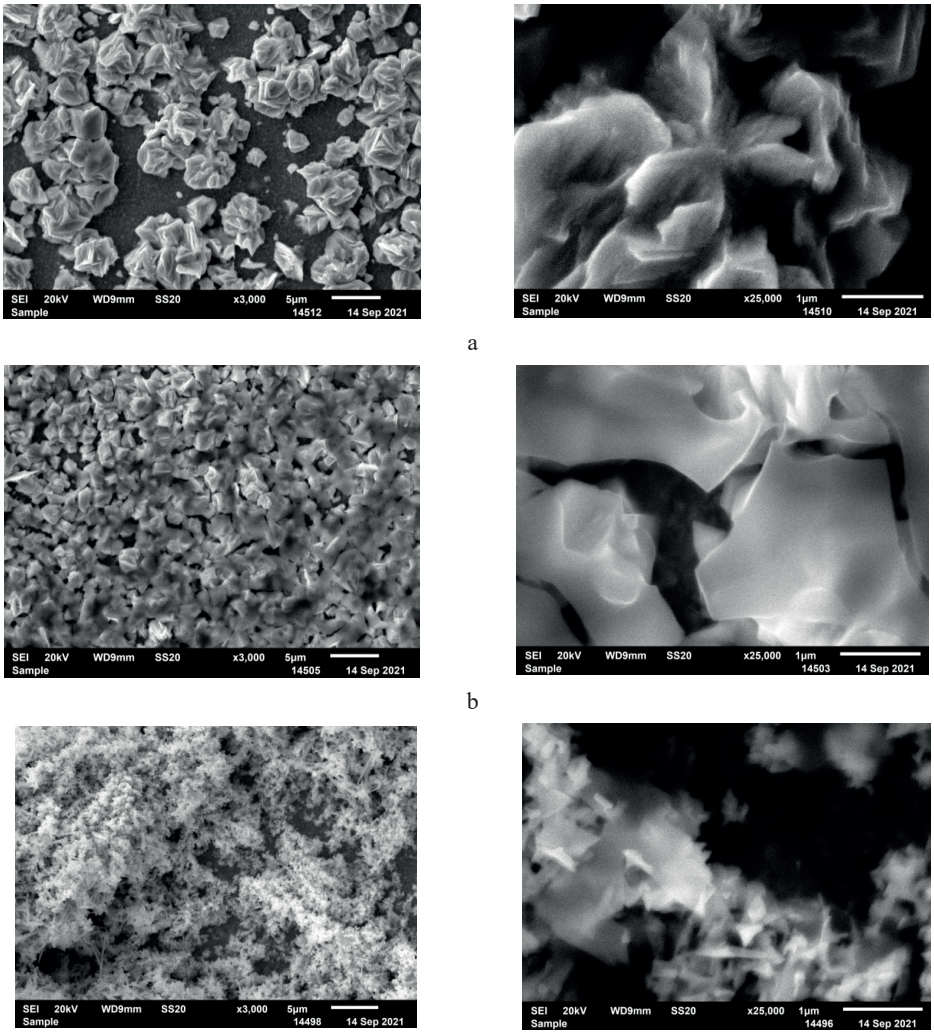

Fig. 8. SEM images of the Bi_2S_3 film obtained by electrodeposition at potentials: a) E = -520 mV; b) E= -535 mV; c) E= -750 mV

According to SEM results (Fig. 8, a.), Bi_2S_3 films deposited at a potential E = -520 mV consist of sharp-angled particles (size 0.5 μm), irregularly covering the substrate surface. The shift of the electrodeposition potential to the negative area (E= -535 mV) contributes to a denser coating of the substrate with Bi_2S_3 particles (Fig. 8, b.). At a potential E = -750 mV, the appearance of feather-like particles observed, which consist of smaller formations (Fig. 8, c.).

According to XRD, Bi_2S_3 thin films deposited at E = -750 mV have the highest content of bismuth sulfide, the lowest amount of crystalline bismuth, and a uniform coating of the substrate surface. These films are used for further photoelectrochemical studies.

PEC measurements

It is preferable to start photoelectrochemical measurements by determining the conductivity and flat band potential (E_{fb}). The study of these parameters will help to determine the band structure of the semiconductor compound, and its ability to absorb and conversion of solar radiation. Photoactivity under visible light of bismuth sulfide thin film obtained at E = -750 mV was carried out by studying the effect of illumination (xenon lamp, 100 mW/cm^2) on the open circuit potential (E_{OC}) of the Bi_2S_3 electrode in 0.5 M Na_2SO_4 (Fig. 9).

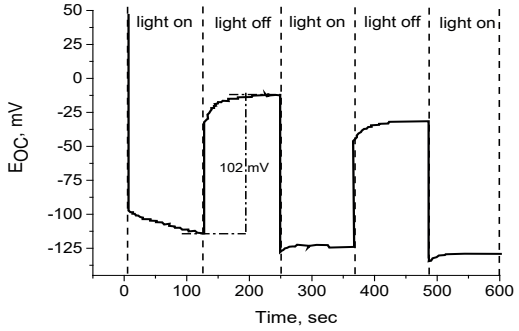

Fig. 9. Time dependence of the open circuit potential of the Bi_2S_3/FTO electrode in the presence and absence of illumination in 0.5 M Na_2SO_4

The measurement of the open circuit potential E_{OC} in 0.5 M Na_2SO_4 solution under chopped illumination (Fig. 9.) showed the decrease of E_{OC} from 50 mV to -114 mV under illumination. This decrease is due to the collection of electrons in the balk of semiconductor film. Under darkness conditions, the E_{OC} value increases to more positive value (-12 mV). The decrease in the value of the open circuit potential under illumination of Bi_2S_3 electrode confirms its photoactivity in the visible solar spectrum and n-type conductivity. After turning off the light source, the photoinduced electrons slowly release and recombine with holes. The rate of decrease in E_{OC} to the equilibrium potential in the dark characterizes the lifetime of photoinduced electrons. A slow decrease in this value indicates that photoinduced electrons can exist longer and transport electrons across grain boundaries. The flat band potential of the Bi_2S_3 photoelectrode (vs Ag/AgCl) is E_{fb}

= -112 mV. The difference between the open circuit potential V_{OC} in the dark and under illumination is the photovoltage, which is found about V_{ph} = 102 mV.

The photoresponse and stability of Bi_2S_3 films, obtained at E= -750 mV, was studied by obtaining photocurrent density–time curves under 0 mV bias conditions in 0.5 M Na_2SO_4 (Fig. 10.) solution.

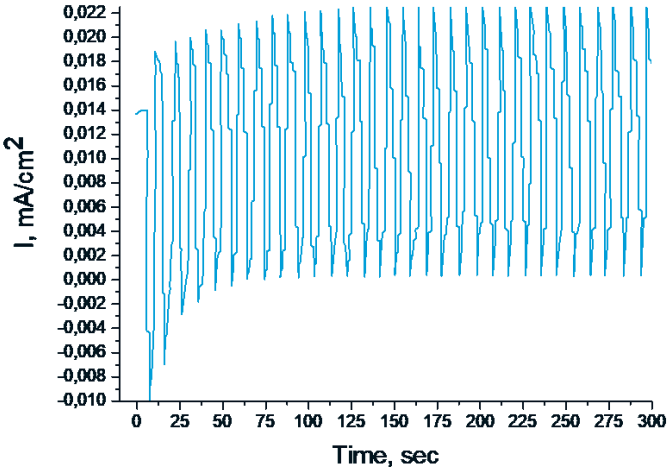

Fig. 10. Stability measurements of the Bi_2S_3/FTO electrode in the presence and absence of illumination in 0.5M Na_2SO_4

Bi_2S_3 film shows the stable photocurrent I_{ph} = 22 μA/cm^2 (Fig. 10). Under illumination, the Bi_2S_3 film showed a photo-response in the form of anode current. In the dark, the photocurrent decreases rapidly. The value of photocurrent increases relative to the initial value, and remains constant (I_{ph} = 22 μA/cm^2). The appearance of a cathodic dark photocurrent in first seconds is associated with the formation of sulfite, according to the reaction 5:

$$SO_3^{2-} + H_2O + 2h^+ = SO_4^{2-} + 2H^+ \quad (5)$$

The results shows good photostability of Bi_2S_3 films in Na_2SO_4 electrolyte, and demonstrates the ability to use Bi_2S_3 films as high sensitivity photodetectors, photoelectronic devices and switches.

Conclusion

In summary, a large experimental work has been carried out to study the electrochemical behavior of bismuth and sulfur ions in aqueous acidic electrolytes based on 10% HNO_3 and electrolytes with additions of the complexing agent $9 \cdot 10^{-3}$ M EDTA-Na. The joint reduction of Bi(III) and S(II) ions on a glassy carbon electrode and on FTO/glass electrode in a $9 \cdot 10^{-3}$ M EDTA-Na solution is investigated. Based on the study of the electrochemical behavior of Bi(III) and S(II) ions in various solutions, the deposition potentials for film synthesis were selected.

The synthesis was carried out in an electrolyte with the addition of EDTA (pH=4) as a complexing agent at potentials E= -520, -535 and -750 mV during 30 minutes. XRD and SEM confirmed the surface morphology and structure of the obtained films. The photoelectrochemical properties of Bi_2S_3 films were studied using PEC method. The registration of the anode photocurrent indicates the n-type conductivity. The photoresponse and stability of Bi_2S_3 films were measured in 0.5 M Na_2SO_4 solution, and showed I_{ph} = 22 μA/cm^2. The obtained results demonstrate the possibility of using Bi_2S_3 films as highly sensitive photodetectors, photoelectronic devices and switches.

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