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Д.В.Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

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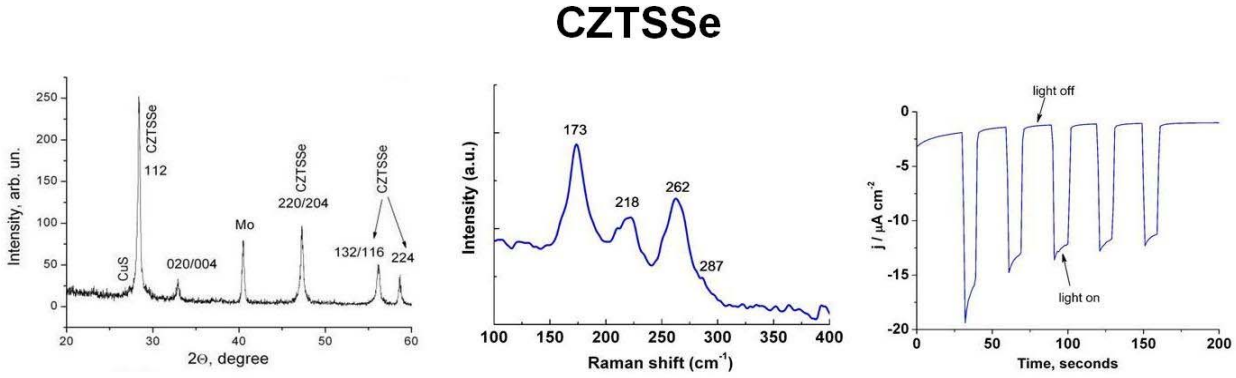
STRUCTURE AND PHOTOELECTROCHEMICAL PROPERTIES OF ELECTRODEPOSITED $Cu_2ZnSn(S,Se)_4$ FILMS

Abstract. A one-step electrochemical synthesis of $Cu_2ZnSnSe_4$ (CZTSe) and Cu_2ZnSnS_4 (CZTS) films on Mo-coated glass from aqueous electrolytes containing both Cu^{+2}, Zn^{+2}, Sn^{+2} and Se^{+4} or S^{+4} ions has been developed. Electrodeposition was performed at a constant potential with subsequent annealing at a temperature of 450 °C in air for 60 minutes. $Cu_2ZnSn(S_{0.96},Se_{0.04})_4$ films were obtained by sulfurizing electrodeposited $Cu_2ZnSnSe_4$ layers in a sulfur atmosphere at 500 °C for 60 minutes. The structure and phase composition of the films was confirmed by XRD and Raman spectroscopy. It was confirmed by the PEC method that all films had p-conductivity. It was established that a change in the chemical composition of the films affects the electrophysical properties, and for $Cu_2ZnSn(S,Se)_4$ layers the photoresponse was 5-6 times higher than for four component compounds.

Key words: electrodeposition, CZTSSe, kesterite, thin film, photoelectrochemistry.

Graphical Abstract



Introduction

Recent progress in creating solar photovoltaic cells based on four-component semiconductors $Cu(In,Ga)Se_2$ (CIGS), Cu_2ZnSnS_4 (CZTS) stimulates researchers to further develop the technology of growing more advanced and efficient thin-film structures [1, 2]. It is known that polycrystalline thin films of the compounds Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ and $Cu_2ZnSn(S_xSe_{1-x})_4$ with the structure of kesterite are promising materials for the production of cheap solar cells. These compounds consist of components that are widespread in nature and can be considered as an inexpensive, affordable material, the use of which does not violate environmental standards, in contrast to frequently used cadmium sulfide, copper-indium selenides, etc. The band gap of these kesterites, depending on the content of sulfur and selenium, can vary

from 0.98 to -1.8 eV, [3, 4], and a high adsorption coefficient ($\alpha = 10^4$ cm^{-1}) for photons with energies greater than width the band gap allows efficient radiation absorption in the chalcogenide layer to be thinner than a few microns. This reduces the amount of material used. Global studies show that the effectiveness of thin-film elements with a material based on multicomponent chalcogenides with a structure of kesterite is continuously increasing [2-5]. An effective solar radiation conversion of 12.6% was reported, which was achieved for the $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solution [5].

The deposition of thin-film absorption layers is often performed using various vacuum techniques at high temperatures. However, single-stage methods of electrodeposition of four and five-component film semiconductors from aqueous electrolytes at low temperatures are attracting more and more attention [6–9].

One of the important applications of multicomponent chalcogenide semiconductors CZTSSe is their use as photocathodes in photoelectrochemical (PEC) decomposition of water. This process attracts attention due to its environmental friendliness and low cost [10, 11]. Methods for the decomposition of water using CZTS photocathodes were developed when they started using compositions of this material with thin layers of sulphides of other metals, for example, cadmium and indium [12]. The CZTS method of electroplating and the subsequent deposition of metal sulfide layers and their activation with platinum are also being successfully used. For example, modification of CZTS by applying a double layer of In_2S_3 / CdS followed by precipitation of a dispersed Pt catalyst made it possible to obtain in the two-electrode PEC process the efficiency of water decomposition equal to 1.63% without any noticeable degradation of the photocathode due to photocorrosion. In_2S_3 films act as mediators for efficient electron transfer on Pt blotches as well as a protective layer to avoid contact between the CdS layer and the external electrolyte solution [13].

In order to develop the technology of using materials based on kesterite to create thin-film photocells or film photocathodes, information on the correspondence of the composition, structure, and optical, in particular, photoelectrochemical properties of these materials, which significantly depend on the production method, is needed [14].

The work of a number of authors [15–21] is devoted to this question. An XRD microstructural analysis for films prepared by magnetron sputtering of metal precursors followed by sulfurization / selenization showed a strong dependence of domain sizes and microstresses on the composition. Domain sizes increased with increasing sulfur content, and selenium-rich films tended to have a more homogeneous domain size distribution. This phenomenon is associated with a lower energy of formation of binary phases with sulfur, which leads to the formation of kesterites, whereas the increase in microstrains is explained by the replacement of large selenium atoms by smaller sulfur atoms in the lattice and the presence of secondary phases. [18].

The method of single-stage electrodeposition of all components at a constant potential from aqueous solutions allows one to reduce the content of double phases in the structure and their influence on the photoelectrochemical properties [5–8].

In this work, the method of potentiostatic deposition of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ from electrolytes containing simultaneously all components is used. The goal of this work is to compare the structural characteristics of CZT(S,Se) films obtained using a single-stage electrodeposition method with subsequent annealing, and their photoelectrochemical properties.

Experimental part

Electrochemical deposition of thin films of compounds Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ was carried out on Mo/glass substrates (working electrode), from aqueous solutions at a constant potential. The potential was maintained using the Gill AC potentiostat-galvanostat from ACM Instruments relative to the Ag/AgCl electrode (KCl sat). A three-electrode thermostatted cell was used. The counter electrode was a platinum coil (or platinum mesh).

Cu_2ZnSnS_4 (CZTS) films were electrochemically precipitated from an electrolyte based on 0.2 M sodium citrate with the addition of 0.1 M tartaric acid and 0.01 M CuSO4 • 5H2O, 0.005 M SnSO4, 0.01 M ZnSO4 • 7H2O, and 0.05 M Na2S2O3 • 5H2O at pH 4.6. The electrolysis was carried out at a constant potential E = -1.0 V with stirring the electrolyte with a magnetic stirrer at room temperature.

Electrodeposition of $Cu_2ZnSnSe_4$ (CZTSe) films was carried out from an electrolyte with a pH of 1.5 based on a solution of 0.1 M tartaric acid, which contained 0.002 M $CuSO_4 \cdot 5H_2O$, 0.01 M $ZnSO_4 \cdot 7H_2O$, 0.01 M $SnCl_4 \cdot 5H_2O$ and 0.005 M $NaHSeO_3$. The electrolysis was carried out at a constant potential E = -0.6 V with stirring the electrolyte with a magnetic stirrer at room temperature.

The obtained samples were washed with distilled water and dried in air. The obtained CZTS and CZTSe films were annealed at a temperature of 450 °C in an atmosphere of air for 30 minutes.

To form the five-component compound $Cu_2ZnSn\ (Se_x,\ S_{1-x})_4$, the process of sulfurization of freshly precipitated thin films $Cu_2ZnSnSe_4$ was carried out. The process was carried out in a quartz tube, where the sample $Cu_2ZnSnSe_4$ and colloidal sulfur were located. Argon was used as the carrier gas. The temperature in the furnace was raised at a rate of 13 °C / min and, after reaching a temperature of 500 ° C, annealing was performed for 60 minutes, then the samples were cooled with the oven to room temperature. After that, the films were not chemically treated. This stage is performed at the State Research Institute for Physical Sciences and Technology, Vilnius.

The study of the structure of the obtained films was performed by the XRD method. XRD spectra were obtained using a SmartLab X-ray diffractometer (Rigaku) at a constant voltage of 9 kW using a rotating Cu anode to study the structure of the samples obtained.

A combined Solver Spectrum system (NT-MDT, Russia) was used to study the Raman spectroscopy method and record the Raman spectra (using a 600/600 grating; 532 nm laser; signal accumulation time 60 seconds). The EDAX method (JSM 6610 LV JOEL, Japan) was used to determine the elemental composition of the electrodeposited CZTS, CZTSe and CZT(S,Se) films after they were annealed.

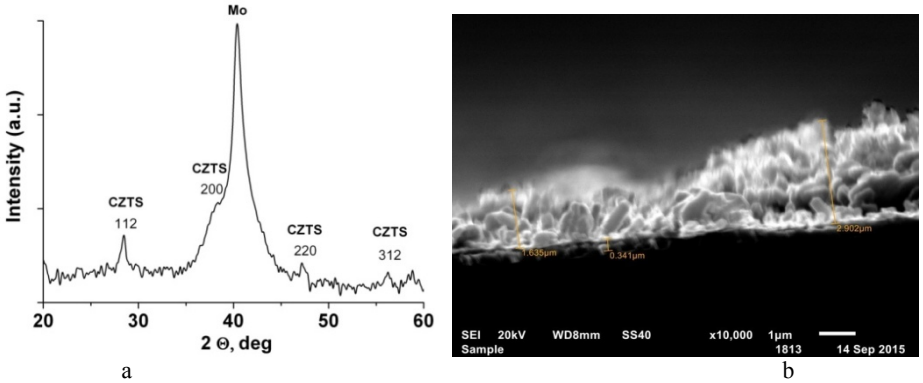
The method of photoelectrochemical (PEC) analysis was performed using a Gill AC potentiostat-galvanostat in a three electrode quartz cell, where the working electrode was made with thin film samples, the platinum coil was used as a counter electrode, and a silver chloride electrode was used as a reference electrode. Photocurrents were recorded in the dark / light mode in a solution of 0.1 M sodium sulfate. A halogen lamp was used as the light source, and the lighting power was 80 mW/cm2.

Results and discussion

Structure analysis

A structural analysis of electrodeposited CZTS films on a Mo/glass substrate and annealed in air at 450 °C was performed using XRD (Fig. 1 (a)). Observed reflexes CZTS kesterite phase and Mo substrate. From the analysis of the diffraction data, it becomes obvious that there are no pronounced reflexes of the double sulfide phases in the electrodeposited films. Estimation of the main peaks corresponds to the provisions 112 and 220 of the kesterite. Peaks are also noted that correspond to the ester levels of 200 and 312. The polycrystalline nature of the precipitates obtained corresponds to the crystal structure of the kesterite [JCPDS card: 26-0575]. Similar results were obtained in [8, 10].

SEM images of deposited CZTS films are shown in Figure 1(b). This picture shows an image in cross-section mode, from which it can be seen that the CZTS film has good adhesion to the glass substrate. CZTS film thickness varies from 0.35 to 2.9 μ.



a b

Figure 1 - (a) XRD spectre and (b) cross-sectional SEM image of CZTS film after annealing

Electrodeposited CZTSe films after annealing were investigated using x-ray diffraction analysis. Figure 2 shows the diffraction patterns before and after annealing. On as-deposited films (Fig. 2, spectrum 1), weak reflections of CZTSe and Mo phases appear (cubic lattice, parameter a = 3.149-3.150 Å). The XRD spectrum of the film after annealing showed three main reflexes at 27.49 °, 45.25 ° and 53.53 °, which correspond well to CZTSe values (ICDD 96-153-1984) with crystalline orientations (112), (220) and (312).

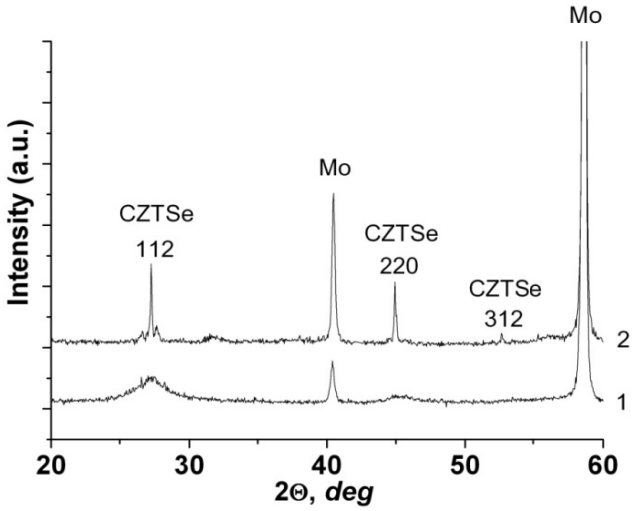
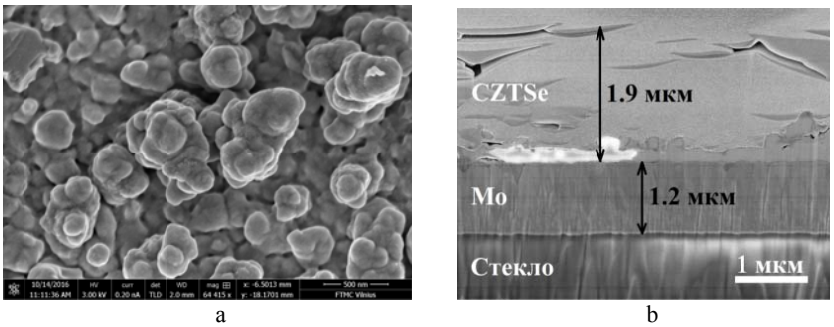


Figure 2 - XRD spectrum of CZTSe films: 1 - before annealing; 2 - after annealing

As can be seen from Fig. 3(a), the grain size and morphology of the film surface is similar to the images obtained in [8] for CZTSe films deposited by an electrochemical method in one stage. The study by the cross-section method showed that the films deposited in our experiments have a maximum thickness of 1.9μ (Fig. 3 (b)).



a b

Figure 3 - SEM images of (a) surface and (b) cross-section of CZTSe/Mo/glass

Immediately after deposition, CZTSe samples were subjected to sulphurization to obtain thin films of the five-component compound CZTSSe. The study of the phase composition of thin films obtained after sulfurizing CZTSe showed the presence of a polycrystalline kesterite phase CZTSSe (Fig. 4). All the dominant diffraction peaks of this film can be attributed to the peaks of the tetragonal structure for CZTSSe: (112), (020/004), (132/116) at 28.4º, 33.05º, 47.39º and 56.15º (ICDD 96- 900-4751). Metal phases other than Mo, as well as intermetallic compounds or oxides were not detected. Detailed analysis of the samples showed that the peak (112) of the CZTSe phase is shifted from 27.49 ° to 28.4 ° due to the partial replacement of Se by S and the formation of the five-component compound CZTSSe. Logarithmic intensity was used to better show low intensity peaks. As can be seen from the fragments of the XRD spectrum, low-intensity peaks can be attributed to the CuS (ICDD 00-085-39280) and ZnS (ICDD 00-002-0564) phases. As well as the presence of double peaks 220/204 and 132/116 at 47.29 º and 56.03 º, confirm the formation of the CZTSSe phase.

All the CZTSSe phase peaks are shifted to large angles, which indicates a decrease in the lattice parameters due to the replacement of Se with S. Given these data, we can conclude that the film was single phase and crystallized in a partially disordered structure of the kesterite.

In addition to the XRD analysis, a combination scattering study (Raman spectroscopy) was performed, which is useful for studying the phase purity and composition of the materials of the kesterite. A simple XRD analysis does not always allow us to determine that a film has a single phase, because many double and triple intermediates have a similar structure and exhibit reflections similar to CZTS (for example, Zn(S)x, Cu2Sn(S)3) [22]. Fig. 5 compares the Raman specters for the three studied compounds CZTS, CZTSe and CZTSSe, obtained using the method of electrodeposition with subsequent annealing.

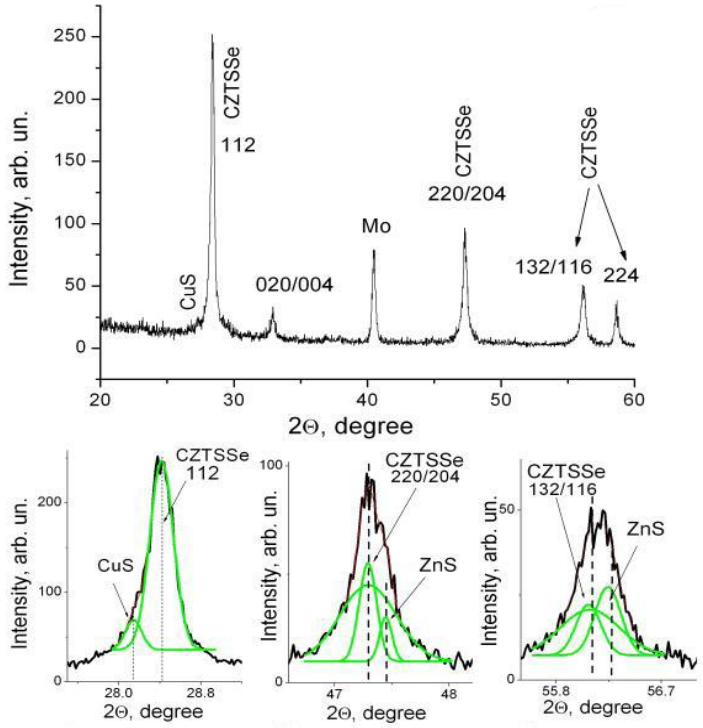
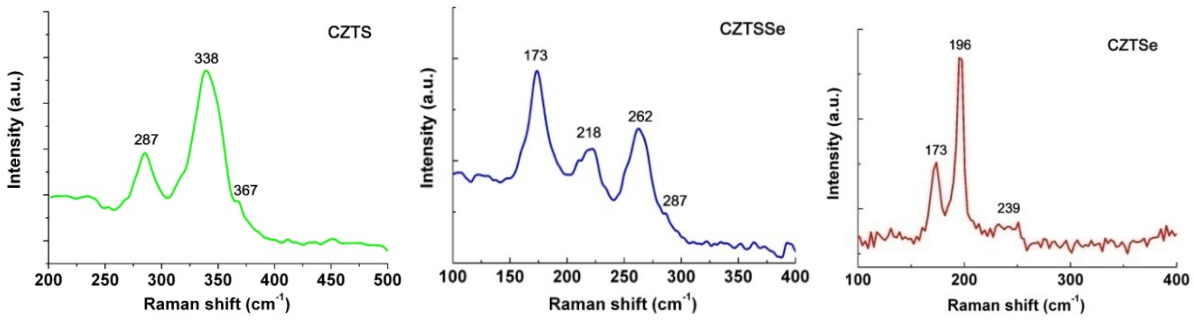


Figure 4 - XRD specter of CZTSSe films

In Fig. 5 (a), the main peaks of the Raman spectrum for CZTS are located around the vibrational mode of the A1 lattice, which reflects the vibrations of the sulfur atom, while the remaining atoms remain fixed. The main peak appears at 338 cm^{-1}, which is consistent with a previously published work for CZTS (338 cm^{-1} main peak with additional peaks at 287, 368 cm^{-1}) [23]. This suggests that under selected conditions of single-stage potentiostatic deposition with subsequent annealing, the compound Cu_2ZnSnS_4 (CZTS) was obtained. Figures 5(b,c) show the Raman specters for the CZT(S,Se) and CZTSe films.



a) b) c)

Figure 5 - Raman specters of kesterite thin films: (a) Cu_2ZnSnS_4 (CZTS); (b) CZTSSe; (c) CZTSe

For the CZTSe compound, the appearance of three peaks was noted (Fig. 5 (c)), where the main vibration mode (196 cm^{-1}) reflects the vibrations of the selenium atom bound to the CZTSe compound. The two main peaks 196 (197) and 173 (170) are most often discussed as the main attributes of the $Cu_2ZnSnSe_4$ structure [19].

For CZT(S,Se) (Fig. 5 (b)), four peaks were found, of which one at 173 cm-1 corresponds to the CZTSe phase and another peak at 287 cm^{-1} corresponds to CZTS, the other two peaks can be attributed to the CZT(S,Se) phase. The strong shifts of the fundamental vibrational modes can be associated with the replacement of Se atoms with a large diameter by small sulfur atoms. The method of Raman scattering refers to the methods of studying the surface with a penetration depth of 100-150 nm with laser energy higher than 2.2 eV [24]. Therefore, the obtained Raman spectra reflect the state of the surface atoms and the structure of the formed films.

To determine the elemental composition of the films obtained, the EDAX method was used (table 1).

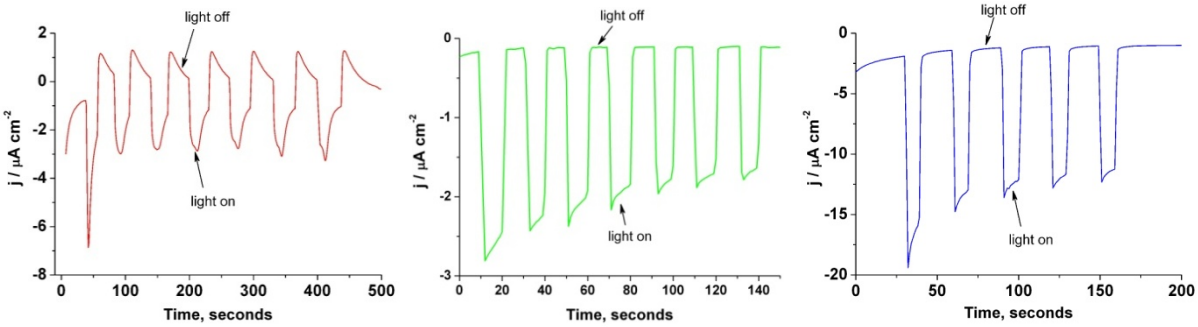
Table 1 - Chemical composition (at.%) of CZTS, CZTSe and CZT(S,Se) thin films

Material	Cu	Zn	Sn	Se	S
CZTS	25.7	11.4	12.4	–	50.3
CZTSe	19.6	10.6	14.6	55.2	–
CZTSSe	13.7	25.98	7.30	1.6	47.5

According to the results of EDX analysis, as a result of sulfurization, a high S/(S+Se) ratio is achieved in films subjected to sulfurization at 500 °C. This ratio remains approximately constant and varies within 0.94 ± 0.02.

Photo electrochemical properties

The photoelectric properties of the obtained materials (CZTSe, CZTS, CZTSSe) were studied using the photoelectrochemical analysis (PEC) method with the Gill AC potentiostat-galvanostat in a three electrode quartz cell, where the working electrode was samples obtained on Mo/glass substrates, the platinum coil served as a counter electrode, a silver chloride electrode (Ag/AgCl, saturated KCl) was used as a reference electrode. Photocurrents were recorded in a solution of 0.1 M sodium sulfate. A halogen lamp (80 mW/cm^2) was used as the light source. The results of the study of photovoltaic properties are presented in Figure 6.



a) CZTSe b) CZTS c) CZTSSe

Figure 6 - Chronoamperometric dependence of the photocurrent of electrodeposited films

The dependence of photocurrent density on time was obtained in the dark / light mode (light off / light on) at a constant potential of -10 mV, which is defined as the stationary potential established between the semiconductor and the electrolyte. The photocurrents of CZTSe films remain constant, while for CZTS they slightly decrease in time and amount to 3 $\mu A/cm^2$ and 2-2.5 $\mu A/cm^2$, respectively. For the CZT(S,Se)/Mo/glass sample, the photocurrent obtained after sulfurization is higher and amounts to ~ 20 $\mu A/cm^2$. Photo corrosion and chemical corrosion are the main problems of semiconductors at PEC, where there is a likelihood of chemical corrosion of the semiconductor surface in the electrolyte. It can be seen

from Fig. 6 (b, c) that the photocurrent gradually decreases, and this is probably due to photo-corrosion S^{2-} from the surface of a thin chalcogenide film, since it is more strongly observed on unprotected CZTS photoelectrodes, similar to observations [17]. Whereas for a sample with a CZTSe film (Fig. 6(a)), the photocurrent remains constant for 500 seconds and longer.

For a five component compound, the decrease in photocurrent over time is less noticeable.

The results obtained indicate that a change in the surface and bulk structure of multicomponent chalcogenide films plays a significant role in changing their photoelectrochemical characteristics.

Conclusion

A comparison of the structural and photoelectrochemical characteristics of multicomponent thin-film chalcogenides CZTS, CZTSe, CZT(S,Se) was made. CZTS, CZTSe thin films were obtained by the method of one-step electrodeposition from aqueous electrolytes on Mo/glass substrates with subsequent annealing in air. Freshly precipitated CZTSe films were subjected to sulphurization in sulfur vapor at 550 ° C. It is shown that all obtained films correspond to polycrystalline kesterite. The formation of the corresponding phases of the quaternary and five-component compounds was confirmed. From the fragments of the X-ray fluorescence analysis of the CZT(S,Se) spectrum, it was established that low-intensity peaks can be attributed to the CuS and ZnS phases. Raman spectra confirm the formation of the CZTS, CZTSe, CZT(S,Se) phases and indicate a significant shift of the Raman spectra for CZT(S,Se), which is associated with the partial replacement of selenium atoms with smaller sulfur atoms. The elemental composition of electrodeposited films corresponds to the phases of the compounds. The ratio S/(S+Se) in films subjected to sulphurization at 500 °C varies within 0.94 ± 0.02. The PEC method determined that the photocurrent for the five-component compound CZT(S,Se) is about 5-6 times higher than for the four-component compounds. A directional change in the microstructural parameters and morphology of the CZT(S,Se) films during their manufacture will be necessary to achieve high efficiency in photoelectrochemical application.

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ЭЛКТРОТҰНДЫРЫЛҒАН $Cu_2ZnSn(S,Se)_4$ ҚАБЫҚШАЛАРЫНЫҢ ҚҰРЛЫМЫ МЕН ФОТОЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТТЕРІ

Аннотация. Cu^{+2}, Zn^{+2}, Sn^{+2}, Se^{+4} немесе S^{+4} иондары бар сулы электролиттерден Мо- қапталған шыныда $Cu_2ZnSnSe_4$ (CZTSe) және Cu_2ZnSnS_4 (CZTS) қабықшаларының бір сатылы электрохимиялық синтезі әзірленді. Электротұндыру үрдісі тұрақты потенциалда орындалды және кейінен 60 минут ішінде 450°C температурасында күйдіру орындалды. Электротұндырылған $Cu_2ZnSnSe_4$ қабаттарын күкірт атмосферасында 60 минут ішінде 500°C -та сульфуризациялау арқылы $Cu_2ZnSn(S_{0,96},Se_{0,04})_4$ қабықшалары алынды. Алынған қабықшалардың құрлымы мен фазалық құрамы РФА мен Раман спектроскопия әдістерімен расталған. Барлық қабықшалар р-өткізгіштікке ие болғаны РЕС әдісімен расталды. Қабықшалардың химиялық құрамының өзгеруі электрофизикалық қасиеттеріне әсер ететіндігі анықталды, ал $Cu_2ZnSn(S,Se)_4$ қабаттарында фотосезімталдығы төрт компонентті қосылыстарға қарағанда 5-6 есе жоғары болды.

Түйін сөздер: электротұндыру, CZTSSe, кестерит, жұқа қабық, фотоэлектрохимия.

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СТРУКТУРА И ФОТОЭЛЕКТРОХИМИЧЕСКИЕ СВОЙСТВА ЭЛЕКТРООСАЖДЕННЫХ ПЛЕНОК $Cu_2ZnSn(S,Se)_4$

Аннотация. Разработан одностадийный электрохимический синтез пленок $Cu_2ZnSnSe_4$ (CZTSe) и Cu_2ZnSnS_4 (CZTS) на стекле, покрытом Mo, из водных электролитов, содержащих одновременно ионы Cu^{+2}, Zn^{+2}, Sn^{+2}, Se^{+4} или S^{+4}. Электроосаждение выполняли при постоянном потенциале с последующим отжигом при температуре 450°C в атмосфере воздуха в течение 60 минут. Пленки $Cu_2ZnSn(S_{0,96}Se_{0,04})_4$ были получены путем сульфуризации электроосажденных слоев $Cu_2ZnSnSe_4$ в атмосфере серы при 500°C в течение 60 минут. Структура и фазовый состав пленок подтвержден методом РФА и спектроскопии комбинационного рассеяния. Методом РЕС подтверждено, что все пленки имели p-проводимость. Установлено, что изменение химического состава пленок влияет на электрофизические свойства, и для слоев $Cu_2ZnSn(S,Se)_4$ фотоотклик оказался в 5-6 раз выше, чем для четрехкомпонентных соединений.

Ключевые слова: Электроосаждение, CZTSSe, кестерит, тонкая пленка, фотоэлектрохимия.

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