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NAS RK is pleased to announce that Bulletin of NAS RK scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of Bulletin of NAS RK in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential multidiscipline content to our community.

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НАН РК сообщает, что научный журнал «Вестник НАН РК» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Вестника НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному мультидисциплинарному контенту для нашего сообщества.

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E-mail: a.k.zhanabaeva@mail.ru**THE ELECTRODEPOSITION OF GALLIUM SELENIDE**

Abstract. The electrochemical deposition of gallium selenide on a glassy carbon electrode from sulphate electrolytes at a constant potential was carried out. The cyclic voltammetric curves of the glassy carbon electrode in two different electrolytes were studied: sulfuric acid and citrate buffer solution containing gallium and selenium ions. The influence of change in the concentration of gallium ions and the deposition potential on the composition of the resulting precipitate is studied. Increasing of the gallium ions concentration from $6 \cdot 10^{-3}$ to $1 \cdot 10^{-1}$ M at a constant concentration of selenium ions $2 \cdot 10^{-3}$ M in the electrolyte leads to an increase in the gallium content in the deposit composition. It is established that in order to obtain the stoichiometric composition of the film, the content of gallium (III) ions in the electrolyte must be many times higher than the content of selenium (IV) ions. The results of elemental analysis of the precipitate confirmed that a film of gallium selenide with a content of 26.7 at% gallium was obtained at a ratio of the concentration of gallium ions and selenium of 50: 1 in the sulphate electrolyte at a potential of -0.8 V. Investigation of the morphology of the surface showed that a uniform coating of the surface of the glassy carbon electrode is achieved at potentials of -0.8 and -0.9 V. X-ray phase analysis confirmed the presence of the Ga_2Se_3 phase in the resulting films.

Keywords: gallium selenide, electrodeposition, voltamperometry.

Introduction. Semiconductor compounds of the III-VI group have attracted great attention of researchers thanks to their suitable structural and optical properties for the application in photoelectronic converters [1]. This group includes gallium monoselenide, GaSe which has hexagonal structure with an optical width of band gap of 2.1 eV and contains Se-Ga-Ga-Se layers and gallium diselenide, Ga_2Se_3 , which has a cubic structure with 1.8-2.6 eV width of band gap [2, 3] and crystallizes in α - and β -structural modifications. In Ga_2Se_3 structure, one third of cationic centers is free and the structure of compound is, therefore, defective. In turn, the defective compound is used in optoelectronic devices for the passivation of heterogeneous compounds, for switching of the memory of light-emitting diodes [4], in combination with GaP substrate [5]. There is a set of methods to obtain gallium selenide. They are the chemical deposition from a vapor phase (CVD) [6], chemical transfer of vapor in vacuum [7], vapor-phase epitaxy [8], heterovalent reaction of V-VI exchange [9], thermal evaporation [10] and molecular beam epitaxy [11, 12]. The most well-known Stokbarger-Bridgmen method [13] of obtaining gallium selenide monocrystals, Ga_2Se_3 is the synthesis at the directed crystallization when a quartz ampoule with the material is stretched in a special furnace and heated to 1473 K with the subsequent slow decrease in temperature. This method requires high purity of materials, and high vacuum and temperature.

Thin Ga_2Se_3 films can be obtained by the zol-gel technique at a crystal formation temperature [14]. Compared to the above-described method, the electrodeposition method from aqueous solutions to obtain thin films on conductive substrates has a number of advantages and is an inexpensive method making it possible to control thickness, morphology and structure of film during deposition [15-17]. In this work, the conditions of gallium selenide electrodeposition on a glassy carbon electrode at a constant potential have been studied.

Methods of study. Voltammetric measurements on a disk glassy carbon electrode with 0.07 cm^2 surface and gallium selenide electrodeposition on flat glassy carbon plates of 1.0 cm^2 area were carried out in a three-electrode thermostatted glassy cell using a silver-chlorine reference electrode and a platinum counter electrode.

Before the experiment, the electrodes were treated with fine abrasive 2000 paper, washed with distilled water and dried in the open air. The sulfate electrolyte with pH = 2.2 (0.45 M Na₂SO₄ + 0.05 M H₂SO₄) and the citrate buffer electrolyte with electrolyte pH = 2.92 were used as background electrolytes. The latter was prepared from 39.3 ml 0.1 M sodium citrate and 60.7 ml 0.1 M HCl. The solutions of gallium and selenium salts (analytically pure), 0.1 M Ga₂(SO₄)₃, 0.1 M NaHSeO₃ and 1 M GaCl₃ were used. The concentration of gallium ions in these electrolytes was changed from 6·10⁻³ to 1.2·10⁻¹ M and the concentration of selenium ions was maintained constant (2·10⁻³ M).

The deposition of gallium selenide was carried out at a constant potential maintained by GillAC potentiostat with Version 5 ACM Instruments software, and at a temperature of 70° C that was maintained by using the LOIP thermostat. The electrolyte mixing was carried out using MM3M magnetic stirrer.

After deposition, the films were washed with distilled water and dried in the open air. Elemental analysis of the contents of components and micrographs of the surface of gallium selenide films were made using the JEOL (Japan "JSM6610 LV") electronic scanning microscope with the capabilities of microanalysis. The phase composition of the films was determined using the DRONE-4/07 instrument with a Co-tube.

Results and Discussion

Voltammetric measurements on a disk glassy carbon electrode. To determine the effect of the concentration of components in the electrolyte on the electrochemical process to reduce the ions, the cyclic voltamperometric dependencies (CVA) of a glassy carbon electrode in a sulfate electrolyte and citrate buffer solution were recorded. The scanning speed of potential was 20 mV/s in the 0 to -1.0 V range and in -1.0 to +1.2 V range in case of inverse scanning. Electrolytes with varying concentrations of gallium ions (6·10⁻³ M, 1.2·10⁻² M, 6·10⁻² M, 8·10⁻² M, 1·10⁻¹ M and 1.2·10⁻¹ M) at a constant concentration of selenium ions (2·10⁻³ M) were investigated.

Figure 1 shows the CVA of a glassy carbon electrode for the reduction of Se(IV) и Ga(III) ions recorded in the sulfate electrolyte. Apparently, the cathode current increases already at 0 V potential indicating the reduction of Se (IV), which starts at more positive potentials. The figure 1 sidebar shows the CVA of Se(IV) (2·10⁻³ M) reduction against the background of sulfate electrolyte taken at a cathode potential scan of +0.3 to -1.0 V. The reduction of Se (IV) is accompanied by the emergence of two peaks at potentials around zero V and at -0.5 V potential. The reduction processes and standard potentials of reactions are described by the equations:

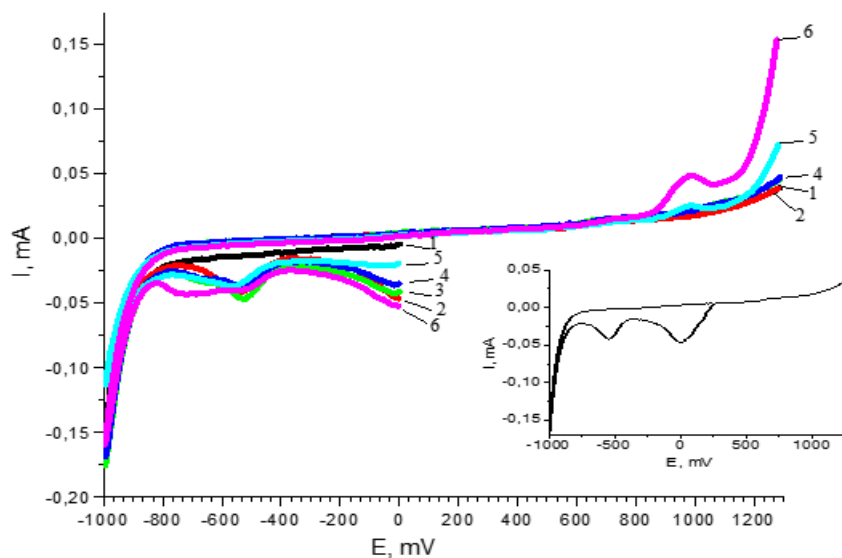


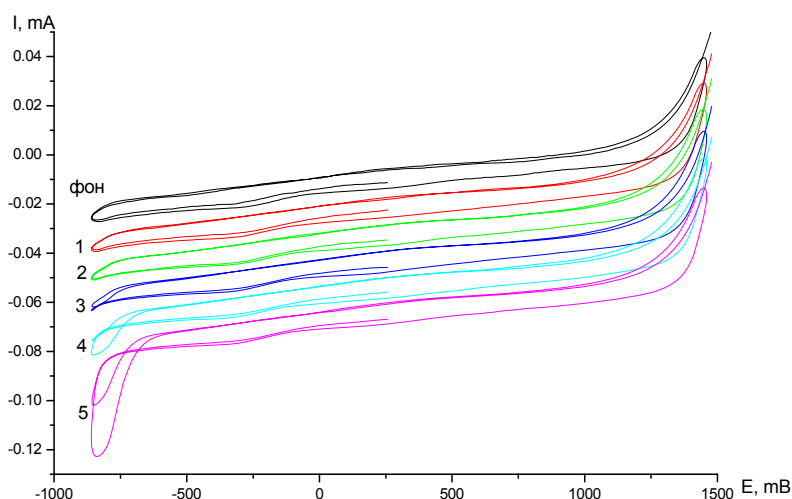
Figure 1 – The CVA of glassy carbon electrode in a sulfate electrolyte at various concentrations of selenium and gallium ions.
 1 – support electrolyte; 2–6 – Se(IV) – 2·10⁻³ M; Ga(III): 3 – 6·10⁻³; 4 – 1.2·10⁻²; 5 – 8·10⁻²; 6 – 1·10⁻¹ M.
 Side bar: Se(IV) – 2·10⁻³ M



In -0.5 V range of potentials, Se (IV) can be reduced according to equation (3) to form selenide ions.

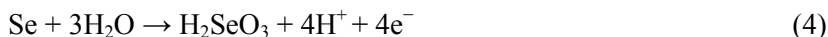
Gallium ions are not reduced on a glassy carbon electrode in the studied range of potentials (figure 2). The CVD of a glassy carbon electrode in a sulfate electrolyte demonstrates the absence of current peaks as the concentration of gallium ions changes from $5 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$ M.

Figure 2 –
The CVA of glassy carbon electrode
in a sulfate electrolyte at a various
content of gallium Ga(III) ions:
1 – $5 \cdot 10^{-4}$; 2 – $1 \cdot 10^{-3}$; 3 – $2 \cdot 10^{-3}$;
4 – $5 \cdot 10^{-3}$; 5 – $1 \cdot 10^{-2}$ M



On adding gallium ions in the electrolyte (figure 1, curves 3-6), the current of the first peak changes, the current peak shape at -0.5 V becomes smooth, and the reduction current lasts until -0.85 V and reaches the hydrogen reduction range.

Analysis of the anode part of CVA testifies that at the maximum content of gallium in the electrolyte equal to $1 \cdot 10^{-3}$ M, a maximum amount of selenium is deposited over the electrode as a compound with gallium. Selenium is oxidized from the compound at potentials close to + 1.0 V.



The results show the formation of a compound to proceed at -0.8 and -0.9 V potentials involving selenide ions due to the chemical reaction of positively charged gallium ions with negatively charged selenium ions.

The CVA in citrate buffer solution shows that in case of joint presence of selenium and gallium ions in the electrolyte the reduction currents increase with an increase in the concentration of gallium. When the content of Ga (III) is from $6 \cdot 10^{-3}$ to $1.2 \cdot 10^{-2}$ M, profile curves coincide with those shown in figure 1 for the sulfate electrolyte. As the concentration of gallium increases (figure 3, curve 3.4) to $8 \cdot 10^{-2}$ M, the reduction currents at $E = -0.5$ V increase and at $E = -0.85$ V there appears an additional distinct current peak that can characterize the reduction of gallium ions on a glassy carbon electrode covered with selenium. Analysis of the anode branch of CVA also indicates that in the process of reduction on the electrode there forms a deposit of selenium compound with gallium, the oxidation potential of which lies within +1.0 V (figure 3).

Based on the results, the -0.8; -0.9 V range of potentials was selected to conduct the potentiostatic deposition of gallium compounds with selenium on a glassy carbon electrode.

Electrodeposition of gallium selenide in sulfate electrolyte. The electrodeposition of gallium ions was carried out at $6 \cdot 10^{-3}$ M concentrations of gallium ions and $2 \cdot 10^{-3}$ M concentrations of selenium ions at -0.8 V potential and 70° C temperature. The resulting film was investigated by electron scanning microscope with the capabilities of microanalysis that showed 0.03 at% content of gallium. Further, the concentration of gallium ions was increased to $1.2 \cdot 10^{-2}$ M, and electrodeposition was carried out at -0.8 and -1.2 V potentials. The elemental composition was studied and micrographs of the surface of resulting films were made (table 1).

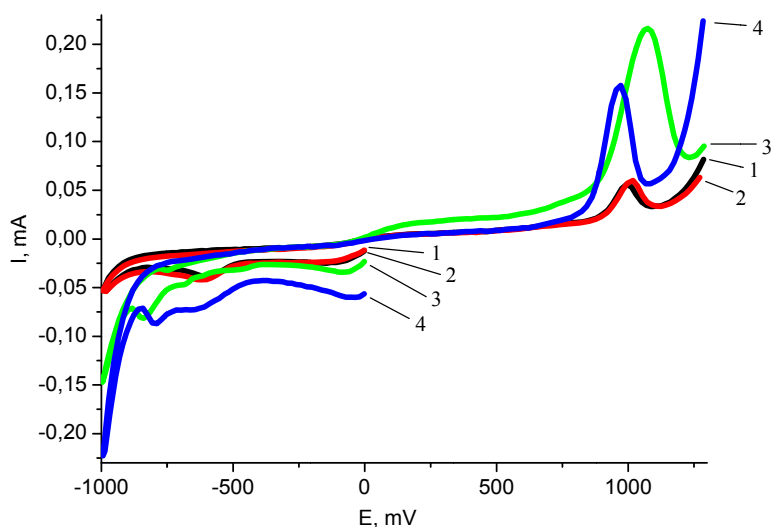


Figure 3 – The CVA of glassy carbon electrode in a citrate buffer solution at a constant concentration of selenium ions and various concentrations of gallium. 1–4 – $\text{Se(IV)}=2 \cdot 10^{-3} \text{ M}$; Ga(III) : 1 – $6 \cdot 10^{-3}$; 2 – $1.2 \cdot 10^{-3}$; 3 – $6 \cdot 10^{-2}$; 4 – $8 \cdot 10^{-2} \text{ M}$

Table 1 – The elemental composition of as-deposited gallium selenide film on glassy carbon at various potentials (at%)

Substrate	Electrodeposition conditions	Electrolyte composition
GC-93	E=-0.8 V T=70°C t = 30 minute	Ga - 0.51% Se - 99.49%
GC-94	E=-1.2 V T=70°C t = 30 minutes	Ga - 0.54% Se - 99.41%

Table 1 shows that the content of gallium in the deposit has increased to ~ 0.5 at%. The shift of reduction potential to the negative side has affected weakly the increase of gallium.

The micrograph of resulting sample surface in figure 4a shows the formation of separate large grains with 4.2- 3.3 μm diameter. The reduction at -1.2 V potential when there starts the parallel reduction of hydrogen, has resulted in disturbance of deposit uniformity due to the formation of filamentary fibers (figure 4b).

In the subsequent experiments, the content of gallium ions in the electrolyte was increased, maintaining a constant concentration of selenium ions equal to $2 \cdot 10^{-3} \text{ M}$. Table 2 shows the results of analysis of the deposited films at -0.8V, -0.9 V and -1.0 V potentials. The best result on the content of gallium, 7.2% is shown by the experiment conducted at -0.8 V potential.

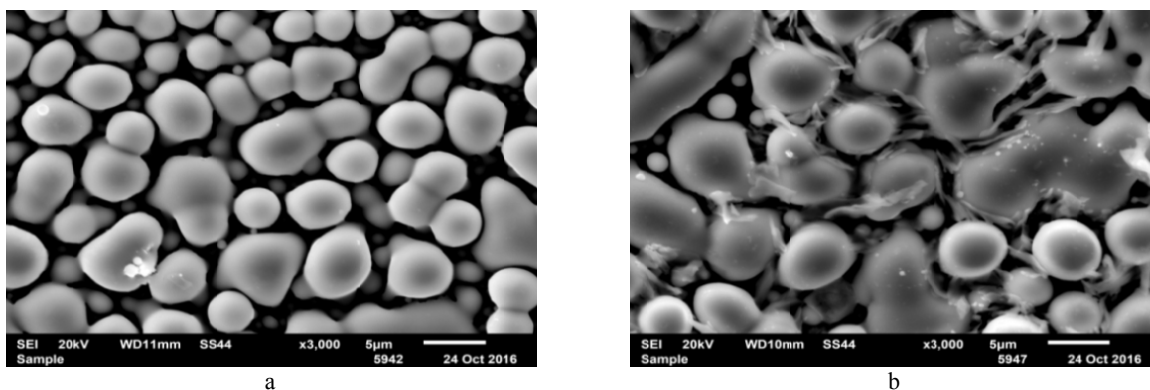
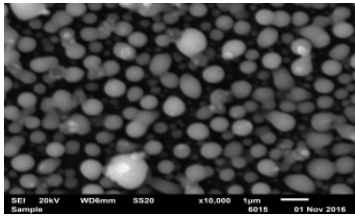
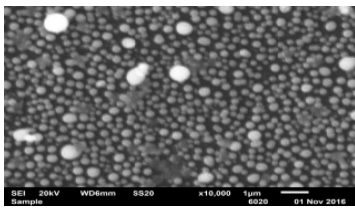
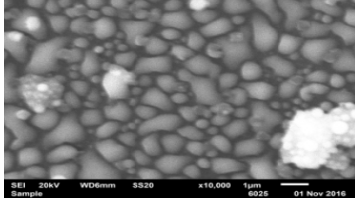


Figure 4 – The micrograph of the surface of films (at 3000 magnification): a – at -0.8V potential; b – at -1.2V potential

Table 2 – The elemental composition of as-deposited gallium selenide film on glassy carbon at various potentials, and the surface micrograph.

Substrate	Electrodeposition conditions	Electrolyte composition	Content in the deposit, at%	Micrographs
GC-95	E=-1.0 V T=70°C t=30 minutes	6·10 ⁻² M Ga ₂ (SO ₄) ₃ 2·10 ⁻³ M NaHSeO ₃	Ga -6.7; Se -93.3	
GC-96	E=-0.9 V T=70°C t=30 minutes	6·10 ⁻² M Ga ₂ (SO ₄) ₃ 2·10 ⁻³ M NaHSeO ₃	Ga - 4.5 Se - 95.5	
GC-97	E=-0.8 V T=70°C t=30 minutes	6·10 ⁻² M Ga ₂ (SO ₄) ₃ 2·10 ⁻³ M NaHSeO ₃	Ga - 7.2 Se - 92.8	

The micrographs in table 2 show that the size grain of the resulting deposit depends on the deposition potential and the content of gallium in the deposited film of gallium selenide.

For further experiments, 1 M GaCl₃ solution was used as a source of gallium ions and their concentration in the electrolyte was increased to 1.0·10⁻¹ M at a constant concentration of selenium ions, 2·10⁻³ M. Electrochemical deposition of gallium selenide was carried out at -0.8 and -0.9V potentials. Cleaned and polished glassy carbon substrates were used. Upon electrodeposition, uniform and thick films of red-brown color were obtained and their composition and surface were studied by the scanning electron microscopy method.

Table 3 – The elemental composition of as-deposited gallium selenide film over glassy carbon at E=-0.8 V and E=-0.9 V potentials within 30 minutes

Substrate	Electrodeposition conditions	Electrolyte composition	Contents of components in the film, at. %
GC-110	E=-0.9 V T=70°C	1·10 ⁻¹ M GaCl ₃ 2·10 ⁻³ M NaHSeO ₃	Ga 15.1 Se 84.9
GC-111	E=-0.9 V T=70°C	1·10 ⁻¹ M GaCl ₃ 2·10 ⁻³ M NaHSeO ₃	Ga 15.9 Se 84.1
GC-112	E=-0.8 V T=70°C	1·10 ⁻¹ M GaCl ₃ 2·10 ⁻³ M NaHSeO ₃	Ga 26.7 Se 73.3

As shown in the table, at -0.8 V potential, within 30 minutes, at a concentration of 1.0·10⁻¹ M GaCl₃ and 2·10⁻³ M NaHSeO₃ on a glassy carbon electrode there forms a film with a maximum content of gallium (26.7 at%). Figure 5 shows a micrograph of the surface of gallium selenide films deposited under the conditions of table 3. One can see that the even distribution of globules is disturbed by the accumulation of coarse crystals consisting of smaller particles. Figure 5b shows the emergence of dendrites in the form of flowers, which is typical for the deposited films of gallium with selenium.

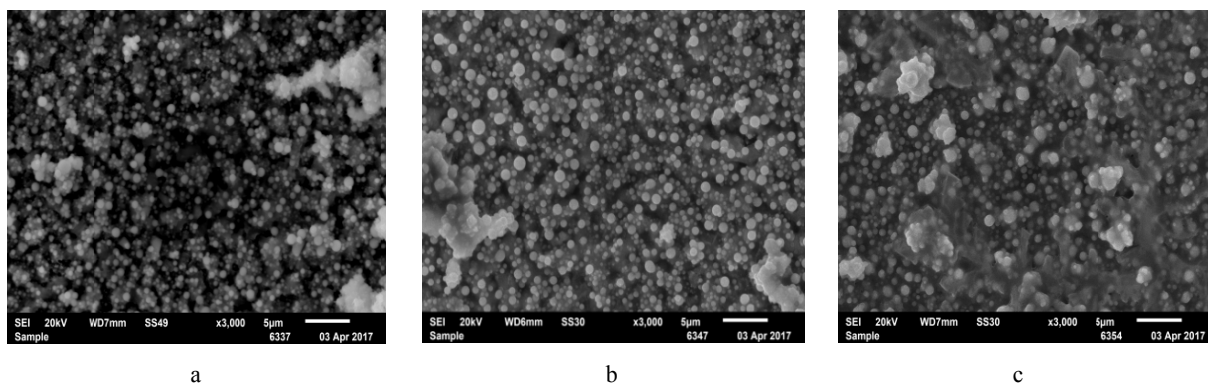


Figure 5 – The micrographs of the surface of films:
 a – $E_{oc} = -0.9V$ on GC-110; b – $E_{oc} = -0.9V$ on GC-111; c – $E_{oc} = -0.8V$ on GC-112

The homogenous formation of spheres with 0.5, 1.1 μm diameter is most typical for the deposits produced by electrodeposition at $E_{oc} = -0.9 V$.

In figure 6, one can see an increase in the content of gallium in the composition of Ga_2Se_3 film at $1 \cdot 10^{-1} M$ $GaCl_3$ concentration in the supporting electrolyte.

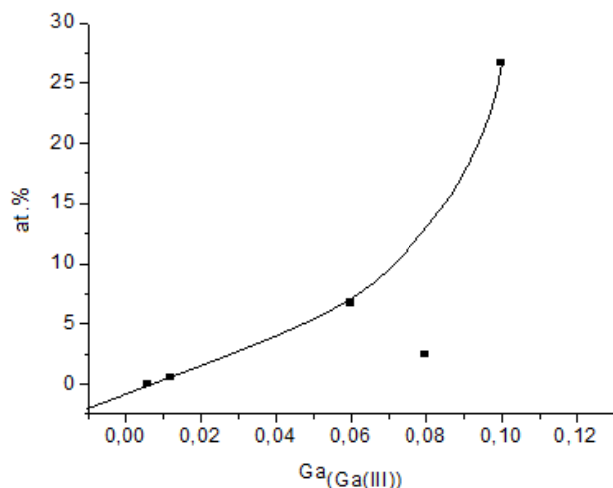


Figure 6 – The dependence of the content of gallium in the deposited film on the concentration of gallium ions in the electrolyte at a constant potential of $-0.8 V$ and $Se=2 \cdot 10^{-3} M$ concentration

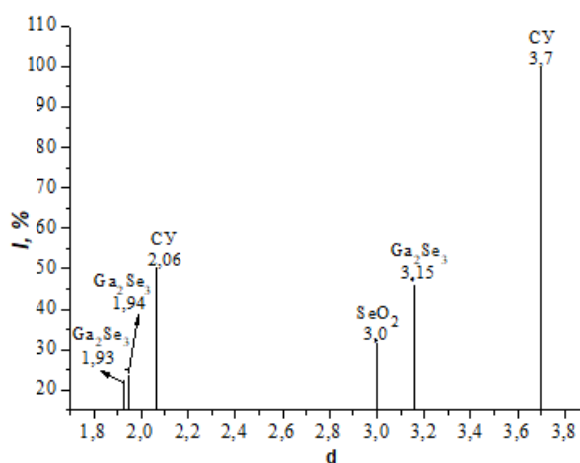


Figure 7 – The dependence of the intensity on the interplanar spacing for GC-112 (glassy carbon sample) (table 3)

Thermal treatment of electrodeposited films. To confirm the phase composition and carry out X-ray phase analysis, the deposited films of gallium selenide were annealed in a muffle furnace in atmospheric air by a two-stage process: first, at $200 \text{ }^\circ C$ during 10 minutes, and the second time at $500 \text{ }^\circ C$ during 15 minutes. After annealing, the film acquired a grey color, the adhesion to substrate was dense, and the surface was homogeneous.

X-ray phase analysis of thin films of gallium selenide electrodeposited on glassy carbon plates was made according to the conditions of table 3. Figure 7 shows the bar radiograph indicating the dependence of the intensity of X-ray reflexes on the interplanar spacings. One can see that graph 7 contains Ga_2Se_3 phase reflexes corresponding to the interplanar spacings 1.93, 1.94, 3.15 according to the ASTM tables. It is noted that the intensity of reflexes increases with an increase in the content of gallium in the deposit. The radiographs also show strong reflexes from the glassy carbon (GC) substrate, since the resulting films do not exceed the thickness of 5 microns. The selenium oxide impurity may indicate the oxidation of a part of selenium on the surface during annealing.

Study on the morphology of the surface of films after thermal treatment was performed using an optical microscope and an atomic-force microscope, JSPM 5200 (JEOL Japan).

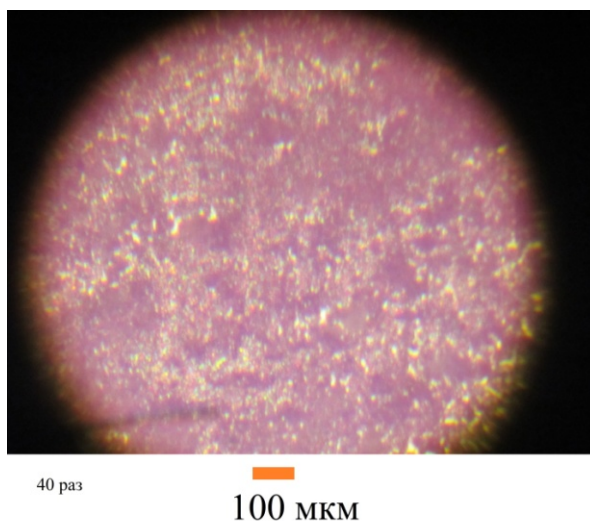


Figure 8 – The pattern of gallium selenide film surface (sample GC-112)

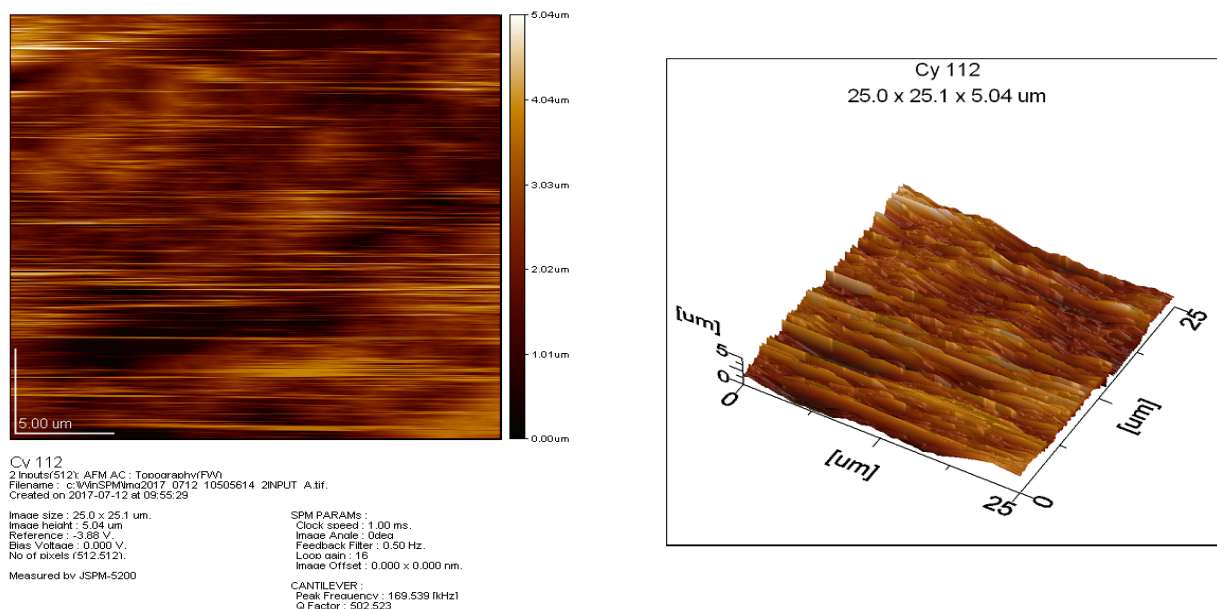


Figure 9 – The pattern of GC-112 sample surface obtained by atomic-force microscopy

The pattern produced by the optical microscope is an evenly coated surface of the deposit (figure 8). The results of atomic-force microscopy (AFM) show that the coat height reaches 5 microns after annealing. The film surface grows in one direction and on the 25x25 μm stretch represents planes growing in parallel.

Conclusions. The electrochemical deposition of gallium selenide on a glassy carbon electrode from sulfate electrolytes at a constant potential has been carried out. Gallium selenide films of up to 5-micron thickness, with the content of 26.7 at% gallium and 73.3 at% selenium have been produced. The composition is close to the stoichiometric composition of Ga_2Se_3 compound. X-ray phase analysis has confirmed the presence of Ga_2Se_3 phase in the resulting films. Study of the surface morphology has shown that uniform coating of the glassy carbon electrode potentials can be achieved at -0.8 and -0.9 V potentials.

Agreement 214-23 with CPCMRA on the topic: «Electrochemical processes fundamentals in electrodeposition of multicomponent semiconductor».

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ГАЛИЙ СЕЛЕНИДІН ЭЛЕКТРОТҰНДЫРУ

Аннотация. Тұрақты потенциалда күкірт қышқылды электролиттен галлий селенидін шыны көміртекті электродта электрохимиялық тұндыру жүргізілді. Шыны көміртекті электродтың циклдік вольтамперлі қисықтары галлий және селен иондары бар екі түрлі электролитте: күкірт қышқылды және цитратты буферлі ертінді де зерттелді. Қабат құрамына галлий ионының концентрациясының өзгерісі мен тұныру потенциалының әсері зерттелді. Галлий ионының концентрациясын $6 \cdot 10^{-3}$ М-ден $1 \cdot 10^{-1}$ М-ге дейін үлкейткенде тұнба құрамында галлийдың максималды құрамына алып келеді, өз кезегінде селен ионының концентрациясы тұрақты $2 \cdot 10^{-3}$ М болып қалады. Стехиометриялыққа құрамдағы қабат алу үшін электролитте галлий ионы (III) селен ионына (IV) қарағанда артығырақ болуы керек. Тұнбаның элементтік анализ нәтижесі күкірт қышқылды электролитте галлий ионының селен ионына қарағанда концентрациясының қатынасы 50:1 болғанда, -0,8В потенциалында құрамында 26,7 ат % галлий бар алынатындығын анықтады. Беттің мор-

фологиясының зерттеулері шыны көміртегі электроды бетінде -0,8 және -0,9 В потенциалдарында біркелкі жабынды түзілетіндігін көрсетті. Рентгенофазалық анализ нәтижесі алынған қабаттарда Ga_2Se_3 фазасының бар екендігін растады.

Түйін сөздер: галлий селениді, электротұндыру, вольтметрметрия.

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ЭЛЕКТРООСАЖДЕНИЕ СЕЛЕНИДА ГАЛЛИЯ

Аннотация. Проведено электрохимическое осаждение селенида галлия на стеклоуглеродном электроде из сернокислых электролитов при постоянном потенциале. Исследованы циклические вольтамперные кривые стеклоуглеродного электрода в двух различных электролитах: сернокислом и цитратном буферном растворе, содержащих ионы галлия и селена. Исследовано влияние изменения концентрации ионов галлия и потенциала осаждения на состав получаемого осадка. Увеличение концентрации ионов галлия от $6 \cdot 10^{-3}$ до $1 \cdot 10^{-1}$ М при постоянной концентрации ионов селена $2 \cdot 10^{-3}$ М в электролите приводит кувеличению содержания галлия в составе осадка. Установлено, что для получения стехиометрического состава пленки содержания ионов галлия (III) в электролите должно во много раз превышать содержание ионов селена (IV). Результаты элементного анализаосадка подтвердили, что при соотношении концентраций ионов галлия и селена 50:1 в сернокислом электролите, при потенциале -0,8В получили пленку селенида галлия с содержанием 26,7 ат% галлия. Исследование морфологии поверхности показало, что однородное покрытие поверхности стеклоуглеродного электрода достигается при потенциалах -0,8 и -0,9В. Рентгенофазовый анализ подтвердил наличие фазы Ga_2Se_3 в полученных пленках.

Ключевые слова: селенид галлия, электроосаждение, вольтметрметрия, тонкие пленки.

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