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CHEMICAL SYNTHESIS OF SOLID SOLUTIONS OF MERCURY SULFIDE-SELENIDE FILMS IN THE PRESENCE OF SODIUM TARTRATE

Solid solutions films of mercury sulfide-selenide ($HgS_{1-x}Se_x$) were synthesized on glass substrates by the chemical bath deposition method. Theoretical calculations of the boundary conditions for the HgS and HgSe formation in the mercury-tartrate-thiourea-selenosulfate system were made. The boundary conditions of $HgS_{1-x}Se_x$ were defined by the overlap area between the constructed HgS and HgSe formation zones. The X-ray diffraction and elemental analysis showed that the obtained films are single-phase and consist of $HgS_{1-x}Se_x$ substitutional solid solutions in zincblende modification. The effect of Na_2SeSO_3 concentration on the degree of S-Se substitution, as well as on the optical and morphological properties of $HgS_{1-x}Se_x$ films, was investigated.

Key words: mercury sulfide; mercury selenide; semiconductor films; solid solution; chemical synthesis; X-ray diffraction; optical spectroscopy.

Introduction

Mercury sulfide (HgS) and mercury selenide (HgSe) belong to the A^2B^6 semiconductor compounds (chalcogenides of the zinc subgroup). HgS and HgSe in the form of coatings or films are difficult to obtain, which has led to the least study of these materials among A^2B^6. The same applies to the intermediate phase, namely the solid solution of mercury selenide sulfide ($HgS_{1-x}Se_x$). It has variable properties, particularly optical and semiconductor, depending on the degree of S-Se substitution (x). If $HgS_{1-x}Se_x$ is obtained in the form of a film with a predictable parameter x, and therefore with predetermined necessary properties, then it will be useful for the manufacture of some optical or electronic devices or their components.

The important point in obtaining the film is the method of its deposition onto substrates. One of the simplest and most cost-effective ways to obtain metal chalcogenide films is through chemical bath deposition [1–3]. In this method, the synthesis reaction takes place in a bath containing dissolved chemical reagents in an aqueous solution at a temperature below the boiling point of water. Films deposition occurs on substrates that are immersed in the bath with the working solution for a certain duration of the process.

The aim of this work is to perform theoretical calculations of the boundary conditions for the formation of HgS and HgSe, as well as $HgS_{1-x}Se_x$ in the mercury-tartrate-thiourea-selenosulfate system. Also, this work aims to carry out X-ray diffraction (XRD), X-ray fluorescence (XRF) elemental analysis, and investigate spectral dependences of optical transmittance and images of scanning electron microscopy (SEM) of the obtained $HgS_{1-x}Se_x$ films.

Materials and research methods

To synthesize $HgS_{1-x}Se_x$ films, the following chemical reagents were used: mercury (II) nitrate ($Hg(NO_3)_2$), sodium tartrate ($Na_2C_4H_4O_6$, Na_2Tart), thiourea ($(NH_2)_2CS$), and sodium selenosulfate (Na_2SeSO_3). Glass plates with unit dimensions of 18·18 mm were used as the substrate material.

The chemical deposition method in the bath was used to synthesize the $HgS_{1-x}Se_x$ films. The necessary amounts of chemicals were dissolved in distilled water to obtain working solutions with the molar concentrations of the components as given in Table 1. After that, the required volume of the working solution was poured into the bath containing the substrates and heated for a specified duration and temperature. When the deposition process was complete, the substrates were removed from the

bath, cleaned by immersing them in distilled water and dried in air.

Table 1

The conditions for the HgS$_{1-x}$Se$_x$ films synthesis

Index	Value
C(Hg(NO$_3$)$_2$), mol/L	0.01
C((NH$_2$)$_2$CS), mol/L	0.02
C(Na$_2$C$_4$H$_4$O$_6$), mol/L	0.25
C(Na$_2$SeSO$_3$), mol/L	0.001–0.005
Volume of working solution, mL	50
Process duration, min	5
pH of working solution	6.8–7.5

X-ray diffraction (XRD) analysis of the synthesized film samples was conducted using an Aeris Research X-ray diffractometer (CuKα⁻ radiation). The experimental diffraction arrays were processed for phase identification using the PowderCell program [4].

Elemental analysis of HgS$_{1-x}$Se$_x$ films was performed using an X-ray fluorescence (XRF) spectrometer ElvaX Light SDD (Elvatech). Quantitative analysis was performed only on the elements Hg, S, and Se. The remaining elements, present as the glass substrate material, were not included in the determination of weight and atomic composition.

The optical spectra of the HgS$_{1-x}$Se$_x$ films T(λ) were recorded in the transmittance (T) vs. Wavelength (λ) dependencies using a Xion 500 spectrophotometer (range 340–900 nm, T accuracy ±0.5 %). The optical band gaps (E_g) were determined from $(\alpha \cdot h\nu)^2$ vs. $h\nu$ dependencies by extrapolating the linear parts of $(\alpha \cdot h\nu)^2$ curves to the intersection with the $h\nu$ (energy axis) [5].

Investigation of the films' surface morphology was carried out using REMMA-102-02 raster scanning electron microscope (SEM).

The pH value of the working solutions was measured with a pH-150 MI pH-meter, using a glass combined electrode.

Results and discussion

Under the given conditions of HgS$_{1-x}$Se$_x$ film synthesis (Table 1), we have an aqueous system of mercury-tartrate-thiourea-selenosulfate. In this system, the HgS$_{1-x}$Se$_x$ formation includes the following main processes: the complexation of Hg^{2+} and the decomposition of thiourea and sodium selenosulfate. Accordingly, the minimum concentration of

mercury (II) salt required for the formation of insoluble HgS and HgSe phases was calculated using the following equations, respectively [6, 7]:

$$C_{Hg^{2+}}^{min} = \frac{SP_{HgS} \cdot [H^+]^2}{\alpha_{Hg^{2+}} \cdot K_{H_2S}^{1,2} \cdot \sqrt{\dfrac{K_{(NH_2)_2CS} \cdot [(NH_2)_2CS] \cdot \beta_{H_2CN_2}}{\beta_{H_2S}}}}, \quad (1)$$

$$C_{Hg^{2+}}^{min} = \frac{SP_{HgSe} \cdot [H^+]}{\alpha_{Hg^{2+}} \cdot K_{H_2Se}^{1,2} \cdot \sqrt{\dfrac{K_{SeSO_3^{2-}} \cdot [SeSO_3^{2-}]}{\beta_{H_2Se}}}}, \quad (2)$$

where $\beta_{H_2Se} = [H^+]^2 + K_{HSe^-}^1 [H^+] + K_{H_2Se}^{1,2}$, $\beta_{H_2CN_2} = [H^+]^2 + K_{HCN_2^-}^1 [H^+] + K_{H_2CN_2}^{1,2}$, $C_{Hg^{2+}}^{min}$ is the minimum concentration of Hg^{2+} ions required for the formation of a solid phase of HgS or HgSe; SP_{HgS} is the solubility product of HgS (equal to $1.6 \cdot 10^{-52}$ [8]); SP_{HgSe} is the solubility product of HgSe (equal to $1 \cdot 10^{-59}$ [7]); $pK_{H_2S}^{1,2}$, $pK_{H_2Se}^{1,2}$, $pK_{H_2CN_2}^{1,2}$, $pK_{(NH_2)_2CS}^{1,2}$, $pK_{SeSO_3^{2-}}$ are dissociation constants of hydrogen sulfide, hydrogen selenide, hydrogen cyanamide, thiourea and selenosulfate, respectively; $\alpha_{Hg^{2+}}$ is the molar fraction of free Hg^{2+} ions in the solution. The value of $\alpha_{Hg^{2+}}$ can be found from the following equation:

$$\alpha_{Hg^{2+}} = \frac{1}{1 + \dfrac{[L]}{K_L^1} + \dfrac{[L]^2}{K_L^{1,2}} + ... + \dfrac{[L]^n}{K_L^{1,2,...,n}}} \quad (3)$$

where [L] is the concentration of the free ligand, and $K_L^{1,2,...,n}$ are constants of the instability of the metal complex forms. In particular, we used the following:

$$K_L^1 (Hg(Tart)) = 10^{-7.0} \text{ [9]},$$

$$pK_L^{1,2} ((Hg((NH_2)_2CS)_2)^{2+}) = 10^{-22.1} \text{ [10, 11]},$$

$$pK_L^{1,2} (Hg(SeSO_3)_2)^{2-}) = 10^{-36.8} \text{ [9]}.$$

Based on the results of calculations using equations (1), (2), and (3) under the conditions given in Table 1, the dependencies of the minimum Hg^{2+} salt concentration required for the formation of insoluble HgS and HgSe phases at various pH values of the working solution were plotted (Fig. 1). It was also determined, as shown in [7], that the formation of the HgO phase should not occur. The boundary conditions of the HgS$_{1-x}$Se$_x$ formation are the overlap area between the constructed HgS and HgSe formation zones. The pH measurement of working solutions indicated pH values from 6.8 to 7.5 with varying Na$_2$SeSO$_3$ concentrations from 0.001 to 0.005 mol/L, respectively. According to this result, the HgS$_{1-x}$Se$_x$ phase can be obtained at the used

0.01 mol/L concentration of mercury (II) salt. However, higher concentrations of Na_2SeSO_3 (> 0.005 mol/L) lead to an increase in the alkalinity of the medium, as well as an increase in the formation rate of the insoluble phase. The latter causes difficulties in obtaining $HgS_{1-x}Se_x$ in the film form, because in this case, it forms practically in precipitate form only.
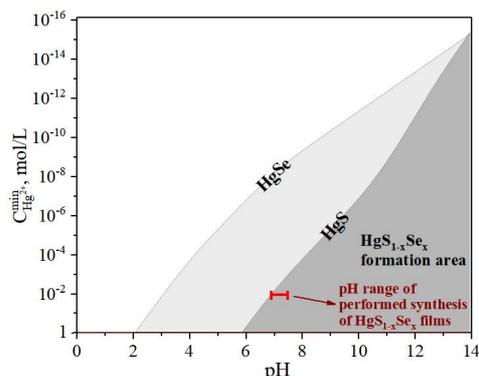
Fig. 1. The boundary conditions of HgS and HgSe formation in the mercury-tartrate-thiourea-selenosulfate system

Thus, in practice, it was possible to obtain films in the measured pH range marked in red in Fig. 1. The X-ray diffraction analysis of the synthesized samples was made (Fig. 2). According to the obtained XRD data, the films are single-phase and have a cubic structure (zincblende, sphalerite [12]). Their peaks are nearly close to the HgS compound (metacinnabar [13]), however, there are some shifts towards peaks of the HgSe compound, which increases within increasing Na_2SeSO_3 concentration in the working solution. This indicates the formation of $HgS_{1-x}Se_x$ substitutional solid solu-

tions with different *x* parameters, which was determined by further XRF analysis.

The elemental analysis of obtained film samples by XRF (Fig. 3, Table 2) shows that $HgS_{1-x}Se_x$ films, obtained at minimal Na_2SeSO_3 concentration (0.001 mol/L), consist of 5.5 at. % of selenium. It corresponds to $x = 0.11$ of the substitutional degree parameter of the $HgS_{1-x}Se_x$ solid solution. The 0.002, 0.003, 0.004 and 0.005 mol/L of Na_2SeSO_3 concentration in working solution leads to 8.8, 14.1, 19.6 and 27.0 at. % of selenium content, respectively (corresponds to $x = 0.176, 0.282, 0.392$ and 0.54, respectively).
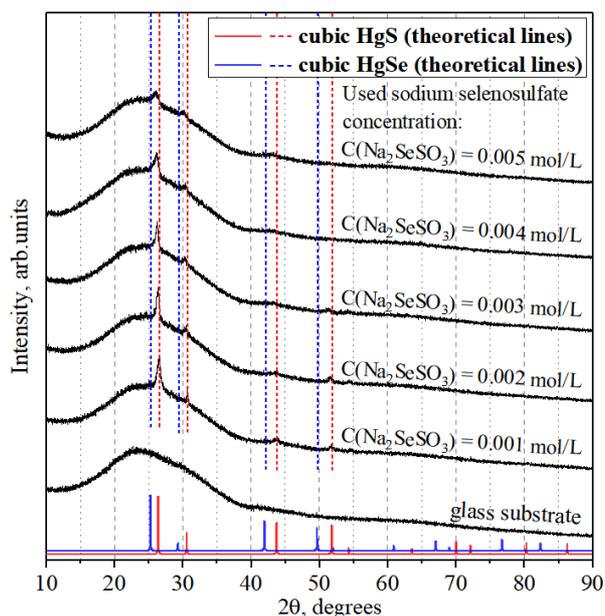
Fig. 2. XRD patterns of $HgS_{1-x}Se_x$ films, deposited at different concentrations of Na_2SeSO_3
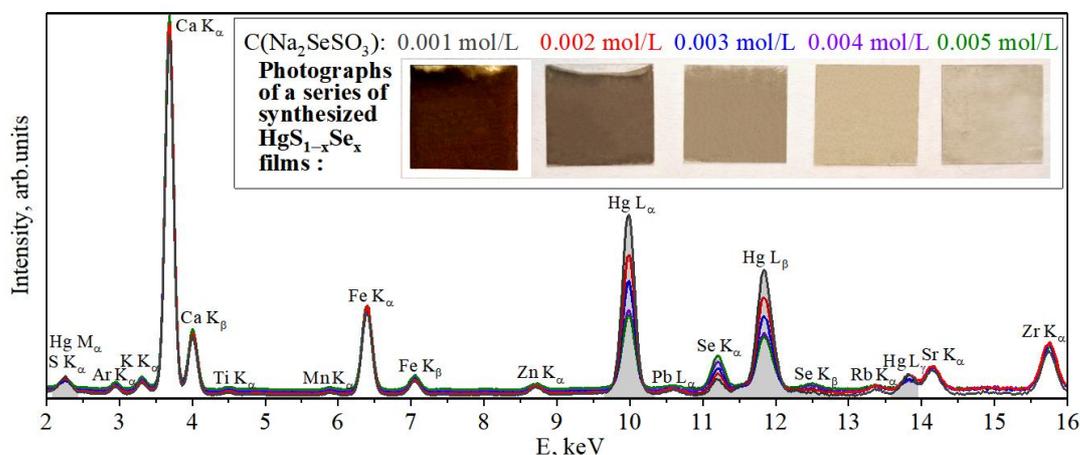
Fig. 3. XRF spectra of $HgS_{1-x}Se_x$ films, deposited on glass substrates at different concentrations of Na_2SeSO_3 (peaks of elements included for quantitative analysis are filled in grey colour)

Results of elemental analysis of HgS$_{1-x}$Se$_x$ films by X-ray fluorescence

Synthesized sample	Used Na$_2$SeSO$_3$ concentration, mol/L	Element	Weight, %	Atomic, %
HgS$_{1-x}$Se$_x$ film	0.001	Hg	84.2	49.6
		S	12.1	44.9
		Se	3.7	5.5
	0.002	Hg	83.1	49.7
		S	11.1	41.5
		Se	5.8	8.8
	0.003	Hg	81.5	49.4
		S	9.3	35.3
		Se	9.2	14.1
	0.004	Hg	79.9	50.1
		S	7.8	30.3
		Se	12.3	19.6
	0.005	Hg	77.6	49.8
		S	5.8	23.2
		Se	16.6	27.0

The optical transmittance spectra T($\perp$) of HgS$_{1-x}$Se$_x$ films obtained at different Na$_2$SeSO$_3$ concentrations in working solution are shown in Fig. 4, *a*. An increase in light transmittance can be observed from the beginning to the end of the λ measurement range. The transmittance curves have jumps or bends located in the wavelength range of approximately 350–500 nm, which is typical for semiconductor films. With the increase of Na$_2$SeSO$_3$ concentration, they are slightly shifted to the longer wavelength region as a result of increasing the selenium amount in deposited HgS$_{1-x}$Se$_x$ films.

The HgS$_{1-x}$Se$_x$ films optical band gap (E_g) (Fig. 4, *b*) numerically increases from 2.62 to 2.85 eV within increasing Na$_2$SeSO$_3$ concentration in

the working solution. The change of E_g can be explained by smooth changes of semiconductor properties with the varies of the x substitutional parameter of HgS$_{1-x}$Se$_x$ films, as well as changes in the amount of deposited film [14], which can be seen in the photographs of the films in Fig. 3.

The SEM results of the surface morphology of HgS$_{1-x}$Se$_x$ films are shown in Fig. 5. A series of microphotographs indicates that HgS$_{1-x}$Se$_x$ films deposited at various Na$_2$SeSO$_3$ concentrations are solid, homogeneous and uniform over the whole surface area and contain a small quantity of precipitate and defects. Their amount decreases with the increasing Na$_2$SeSO$_3$ concentration, as the amount of deposited film also decreases.

a   *b*
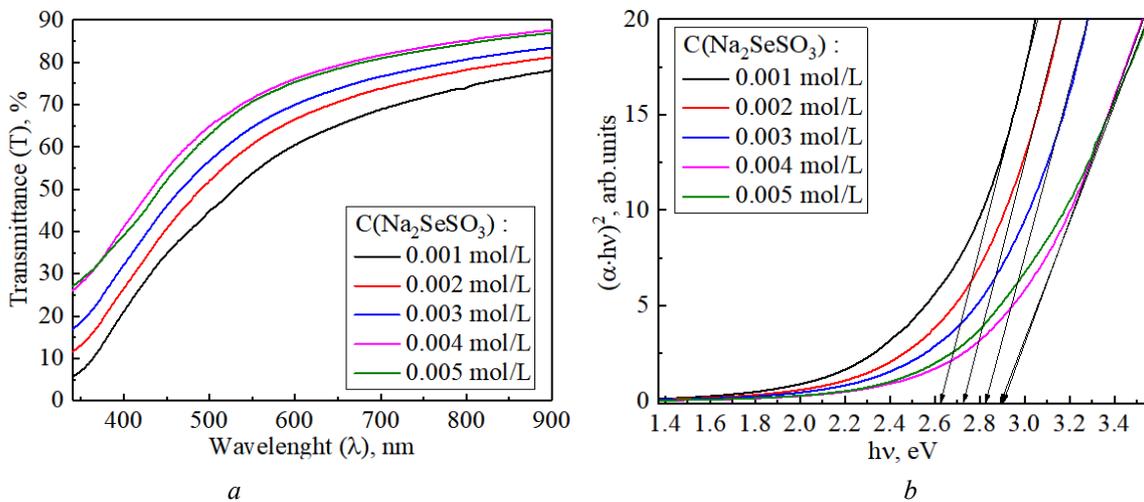
Fig. 4. Optical transmittance spectra of HgS$_{1-x}$Se$_x$ films, deposited at different concentrations of Na$_2$SeSO$_3$

a   *b*   *c*
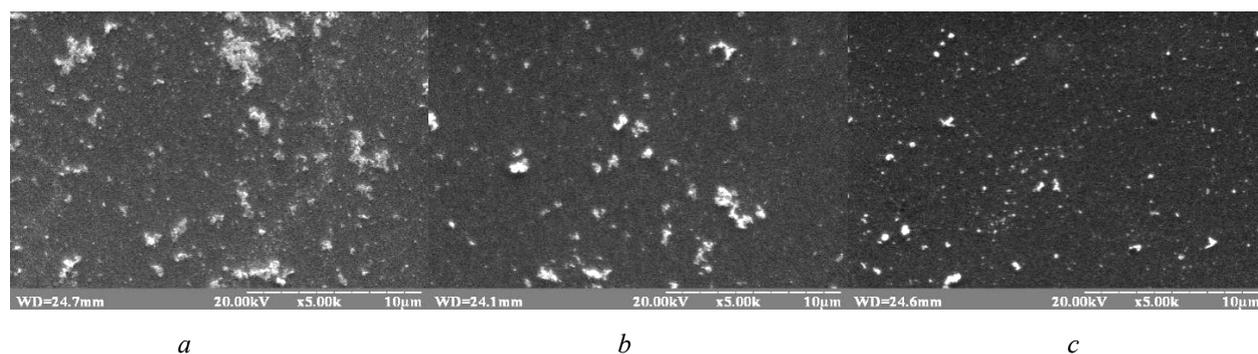
Fig. 5. Surface morphology of HgS$_{1-x}$Se$_x$ films, obtained at different Na$_2$SeSO$_3$ concentrations:
a – 0.001 mol/L; b – 0.003 mol/L; c – 0.005 mol/L

Conclusions

The boundary conditions for the formation of mercury sulfide and mercury selenide were determined in the mercury-tartrate-thiourea-selenosulfate system as well as the HgS$_{1-x}$Se$_x$ formation region.

The HgS$_{1-x}$Se$_x$ solid solutions films were synthesized on glass substrates by chemical bath deposition at different Na$_2$SeSO$_3$ concentrations. It was established that the formation of HgS$_{1-x}$Se$_x$ films (under the given synthesis conditions) occurs in the nearly neutral region of the working solution medium, which is located within the defined area of HgS$_{1-x}$Se$_x$ phase formation.

The effect of Na$_2$SeSO$_3$ concentration on the phase and elemental composition, as well as on the surface morphology and optical properties of the obtained HgS$_{1-x}$Se$_x$ films were studied.

Based on the obtained results of chemical synthesis and studies in this work, the films of HgS$_{1-x}$Se$_x$ solid solution, by their variable semiconductor properties, are promising for manufacturing semiconductor materials or components in various electronic device applications.

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ХІМІЧНИЙ СИНТЕЗ ПЛІВКОВИХ ТВЕРДИХ РОЗЧИНІВ СУЛЬФІДУ-СЕЛЕНІДУ РТУТІ В ПРИСУТНОСТІ ТАРТРАТУ НАТРІЮ

Плівкові тверді розчини сульфіду-селеніду ртуті ($HgS_{1-x}Se_x$) синтезовано на скляних підкладках методом хімічного осадження у ванні. Виконано теоретичні розрахунки граничних умов утворення HgS і HgSe у системі ртуть – тартрат – тіосечовина – селеносульфат. Граничні умови $HgS_{1-x}Se_x$ визначено областю перекриття побудованих зон утворення HgS і HgSe. Рентгенодифракційний та елементний аналіз показав, що отримані плівки є однофазними і складаються із твердих розчинів заміщення $HgS_{1-x}Se_x$ у модифікації цинкової обманки. Досліджено вплив концентрації Na_2SeSO_3 на ступінь заміщення S-Se, а також на оптичні та морфологічні властивості плівок $HgS_{1-x}Se_x$.

Ключові слова: сульфід ртуті; селенід ртуті; напівпровідникові плівки; твердий розчин; хімічний синтез; рентгенівська дифракція; оптична спектроскопія.