UDC 539.232:546:492:546.23

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THE EFFECT OF DIFFERENT COMPLEXING AGENTS ON THE PROPERTIES OF MERCURY SELENIDE FILMS DEPOSITED FROM AQUEOUS SOLUTIONS

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The mercury selenide (HgSe) films were obtained on glass substrates by chemical bath deposition method with using aqueous solutions of mercury (II) nitrate, sodium selenosulfate and complexing agents (potassium thiocyanate, potassium iodide or sodium thiosulfate). In this work, the complex studies were performed, including the theoretical calculation of boundary conditions for the formation of mercury selenide and mercury oxide with various ligands, and the experimental investigation of the composition, structure, optics and morphology of the synthesized HgSe semiconductor films, depending on the effect of three different complexing agents. The obtained films are single-phase and have a sphalerite structure. They have a homogeneous solid surface with the practically stoichiometric composition and a wide interval of the variation of optical band gap. An analysis of the obtained experimental results allows relating the HgSe deposition conditions to the properties of the obtained semiconductor films, revealing the advantages and disadvantages of the used complexing agents and determining the expediency of their use.

Keywords: mercury selenide, semiconductor films, chemical deposition, optical properties, morphology analysis.

Introduction

Mercury selenide (HgSe) belongs to semiconductors of the $A^{II}B^{VI}$ group. Products based on them are technologically interesting materials which can be used in IR detectors, ultrasonic transducers, catalysts, electrostatic reflecting materials and solar cells [1,2]. Unlike chalcogenides of zinc and cadmium, mercury selenide is little-investigated. A technologically convenient way of its production seems to be a chemical bath deposition [3]. Such a synthesis is based on the reactions between a metal salt, complexing agent and chalcogenizer in an aqueous solution. There is no information in the literature on the effect of complexing agents on the synthesis and properties of HgSe films. First of all, this is due to the inability to use typical reagents that have been successfully used for the synthesis of cadmium and zinc chalcogenide films. It is also possible that difficulties arise in the production of HgSe films due to its very small solubility product. Therefore, the development of a simple and reproducible technique for the synthesis of mercury selenide films is an actual task. In the case of HgSe films, it is convenient to use for complexation such reagents as potassium thiocyanate (KSCN), potassium iodide (KI) and sodium thiosulfate ($Na_2S_2O_3$), because they form sufficiently stable complexes with mercury and the most readily available Se-chalcogenizer, sodium selenosulfate (Na_2SeSO_3).

The aim of our work was to conduct complex studies, including the theoretical calculation of the boundary conditions for the formation of mercury selenide and mercury oxide with various complexing agents and the experimental study of the composition, structure, optical properties and morphology of the synthesized HgSe semiconductor films, depending on the effect of different complexing agents. An analysis of the obtained experimental results will allow us to relate the HgSe deposition conditions to the properties of the obtained semiconductor films, to reveal the advantages and disadvantages of the used complexing agents and to determine the expediency of their using. This is an actual task of thin-film technologies, the solution of which will allow controlling the process of chemical deposition of mercury selenide films.

Experimental

For the synthesis of HgSe films, freshly prepared solutions of 0.05 M mercury (II) nitrate ($Hg(NO_3)_2$),

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complexing agent and 0.25 M sodium selenosulfate (Na_2SeSO_3) were used. 2.0 M solution of potassium thiocyanate (KSCN), 0.1 M potassium iodide (KI) and 1.0 M sodium thiosulphate ($Na_2S_2O_3$) were used as complexing agents. If necessary, trisodium citrate ($Na_3C_6H_5O_7$) 1.0 M solution was used as a pH regulator. A solution of sodium selenosulfate was prepared by adding powdered selenium to an aqueous solution of sodium sulfite (Na_2SO_3) and refluxing for 3 hours.

The chemical bath depositions of HgSe films were carried out on pre-cleaned glass substrates (18r18 mm). To this end, a working solution was prepared by successive addition of freshly prepared aqueous solutions of the mercury salt, a complex reaction agent, chalcogenizing reagent and distilling water, the solution being stirred. The deposition was performed in a glass bath; after that the substrates were removed, washed with distilled water and dried in air.

The compositions of working solutions with various complexing agents were different. The following order of working solutions corresponds to the order of mixing of the reagents.

Working solution No. 1: 40 ml of 0.05 M $Hg(NO_3)_2$ solution, 100 ml of 2.0 M KSCN solution, 52 ml of distilled water and 8 ml of 0.25 M Na_2SeSO_3 solution. The volume of the solution is 200 ml. The deposition was carried out for 10–80 min at room temperature (293 K).

Working solution No. 2: 40 ml of 0.05 M $Hg(NO_3)_2$ solution, 80 ml of 0.1 M KI solution, 72 ml of distilled water and 8 ml of 0.25 M Na_2SeSO_3 solution. The total volume of the solution is 200 ml. The deposition was carried out for 2–10 min at a temperature of 363 K. In this case, an increased temperature is used during the synthesis; this is due to the fact that a significant amount of mercury iodide-selenide $Hg_3I_2Se_2$ may be formed as a by-product at 293 K, as was previously shown [4].

Working solution No. 3: 40 ml of 0.05 M of $Hg(NO_3)_2$ solution, 20 ml of 1.0 M $Na_3C_6H_5O_7$ solution, 100 ml of 1.0 M $Na_2S_2O_3$ solution, 32 ml of distilled water and 8 ml of 0.25 M Na_2SeSO_3 solution. The total volume of the solution is 200 ml. The deposition was carried out for 20–220 minutes at room temperature (293 K). In this case, the ($Hg(NO_3)_2$) solution was acidic before the mixing with sodium thiosulfate (pH~4.3); thus, the mercury salt was neutralized with trisodium citrate (to pH>7) to prevent the decomposition of $Na_2S_2O_3$ ($S_2O_3^{2-}+2H^+ \rightarrow S^0\downarrow+SO_2+H_2O$) [5].

The synthesized samples of HgSe films were dark brown. Their adhesion to the glass substrate was weak. The films were easily removed by applying only small mechanical forces. In the case HgSe films obtained using Na_2SeSO_3 and KI, a mirror hue was observed, which was absent in the case of KSCN.

The pH values of the working solutions were measured using an ionometer pH-301.

The XRD analysis of the investigated samples was performed using DRON–3.0 diffractometer (CuK_α–radiation). The primary treatment of diffractograms for the identification of phases was conducted by using PowderCell program [6]. The unit cell parameters were calculated by the FullProf software package [7].

The optical absorption spectra of the films were measured with Xion 500 «Dr. Lange» spectrophotometer in the wavelength range of 340–900 nm. The optical transmission accuracy was ±0.5%.

The investigation of the films surface morphology was carried out using a scanning electron microscope REMMA-102-02 with a microanalysis system.

Results and discussion

The synthesis of mercury selenide films in an aqueous solution includes the following main processes: the complexation of Hg^{2+} and the decomposition of sodium selenosulfate. Let us consider these processes to determine the boundary conditions of the HgSe formation. Equations and mathematical concepts to perform these actions are analogous to those from the works of the authors [8,9], where the formation of cadmium and lead sulfides and selenides is considered using such chalcogenizators as thiourea and selenourea.

The process of decomposition of selenosulphate can be written by the following equation:

$$SeSO_3^{2-} + H_2O \rightleftarrows H_2Se + SO_4^{2-}\ . \qquad (1)$$

The equilibrium constant of this process can be given as:

$$K_{SeSO_3^{2-}} = \frac{[H_2Se]\cdot[SO_4^{2-}]}{[SeSO_3^{2-}]}\ . \qquad (2)$$

Hydrogen selenide (H_2Se) is a weak acid, then its dissociation constant will be as follows:

$$K^{1,2}_{H_2Se} = K^{1}_{HSe^-}\cdot K^{2}_{Se^{2-}} = \frac{[H^+]^2\cdot[Se^{2-}]}{[H_2Se]}\ . \qquad (3)$$

This acid will be present in solution in the form of H_2Se molecules and HSe^-, Se^{2-} ions. Their total concentration according to Eq. (1) will be numerically equal to the concentration of sulfate ions:

$$C_0 = [H_2Se]+[HSe^-]+[Se^-]=[SO_4^{2-}]\,. \qquad (4)$$

The molar fractions of the undissociated H_2Se and the HSe^-, Se^{2-} ions in the solution will be as follows:

$$\alpha_{H_2Se}=\frac{[H_2Se]}{C_0}=\frac{[H^+]^2}{\beta_{H_2Se}}\,, \qquad (5)$$

$$\alpha_{HSe^-}=\frac{[HSe^-]}{C_0}=\frac{K^1_{HSe^-}[H^+]}{\beta_{H_2Se}}\,, \qquad (6)$$

$$\alpha_{Se^{2-}}=\frac{[Se^{2-}]}{C_0}=\frac{K^{1,2}_{H_2Se}}{\beta_{H_2Se}}\,, \qquad (7)$$

where $\beta_{H_2Se}=[H^+]^2+K^1_{HSe^-}[H^+]+K^{1,2}_{H_2Se}$.

If we take into account Eqs. (3)–(5), (7), we can transform Eq. (2) into the following form:

$$K_{SeSO_3^{2-}}=\frac{[H_2Se]\cdot[SO_4^{2-}]}{[SeSO_3^{2-}]}=\frac{[H^+]^2\cdot[Se^{2-}]\cdot C_0}{K^{1,2}_{H_2Se}[SeSO_3^{2-}]}=$$

$$=\frac{[H^+]^2\cdot[Se^{2-}]}{K^{1,2}_{H_2Se}[SeSO_3^{2-}]}\cdot\frac{[Se^{2-}]}{\alpha_{Se^{2-}}}=\frac{[H^+]^2\cdot[Se^{2-}]^2\cdot\beta_{H_2Se}}{(K^{1,2}_{H_2Se})^2[SeSO_3^{2-}]}\,. \qquad (8)$$

Using Eq. (8), we can find the initial concentration of selenium ions in the solution, depending on the concentration of selenium sulfate and the acidity of the medium:

$$[Se^{2-}]=\frac{K^{1,2}_{H_2Se}}{[H^+]}\sqrt{\frac{K_{SeSO_3^{2-}}\cdot[SeSO_3^{2-}]}{\beta_{H_2Se}}}\,. \qquad (9)$$

Mercury forms complex compounds with many substances. The use of ligands of different stability allows adjusting the concentration of uncomplexed mercury ions in the working solution. Their initial concentration in solution will be as follows:

$$[Hg^{2+}]=C_{Hg^{2+}}\cdot\alpha_{Hg^{2+}}\,, \qquad (10)$$

where $C_{Hg^{2+}}$ is the initial concentration of Hg^{2+} salt, $\alpha_{Hg^{2+}}$ 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:

$$\alpha_{Hg^{2+}}=\frac{1}{1+\frac{[L]}{K^1_L}+\frac{[L]^2}{K^{1,2}_L}+\ldots+\frac{[L]^n}{K^{1,2,\ldots n}_L}}\,, \qquad (11)$$

where [L] is the concentration of free ligand, and $K^{1,2,\ldots n}_L$ is the instability constants of the metal complexes.

The formation of insoluble mercury selenide occurs according to the equation:

$$Hg^{2+}+Se^{2-}\rightarrow HgSe\downarrow\,. \qquad (12)$$

The following expression of the solubility product (SP_{HgSe}) [10] gives a necessary condition for its passage:

$$SP_{HgSe}=[Hg^{2+}]\cdot[Se^{2-}]\geq 1\cdot 10^{-59}\,. \qquad (13)$$

Substituting Eqs. (9) and (10) into Eq. (13) and taking the concentration of the mercury salt in the working solution at the lowest level which is required to achieve the solubility product of the mercury of selenide ($C_{Hg^{2+}}=C^{min}_{Hg^{2+}}$), we can obtain:

$$SP_{HgSe}=C^{min}_{Hg^{2+}}\cdot\alpha_{Hg^{2+}}\cdot\frac{K^{1,2}_{H_2Se}}{[H^+]}\sqrt{\frac{K_{SeSO_3^{2-}}\cdot[SeSO_3^{2-}]}{\beta_{H_2Se}}}\,. \qquad (14)$$

Expressing $C^{min}_{Hg^{2+}}$ from Eq. (14), we get:

$$C^{min}_{Hg^{2+}}=\frac{SP_{HgSe}\cdot[H^+]}{\alpha_{Hg^{2+}}\cdot K^{1,2}_{H_2Se}\cdot\sqrt{\frac{K_{SeSO_3^{2-}}\cdot[SeSO_3^{2-}]}{\beta_{H_2Se}}}}\,. \qquad (15)$$

Finding the logarithm Eq. (15) gives the following expression:

$$pC^{min}_{Hg^{2+}}=pSP_{HgSe}+pH-p\alpha_{Hg^{2+}}-pK^{1,2}_{H_2Se}-$$

$$-\frac{1}{2}\left(pK_{SeSO_3^{2-}}+p[SeSO_3^{2-}]-p\beta_{H_2Se}\right)\,, \qquad (16)$$

where p is the indicator (negative decimal logarithm).

When synthesizing HgSe in alkaline media, the following side processes are possible:

$$Hg^{2+}+2OH^-Hg(OH)_2\rightarrow HgO\downarrow+H_2O\,. \qquad (17)$$

Based on literature data [9], the minimum concentration of mercury salt that is required for the formation of mercury oxide as a by-product (Eq. (17)), can be found by the following equation:

$$pC^{min}_{Hg^{2+}} = pSP_{Hg(OH)_2} - p\alpha_{Hg^{2+}} - 2pK_{H_2O} + 2pH. \quad (18)$$

On the basis of Eqs. (16) and (17), the dependences of the minimum concentration of mercury salt required to form HgSe and HgO at the pH value of the working solution were proposed (Fig. 1). The calculations were carried out at the values of the constants given in Table 1. The ions of thiocyanate, iodide and thiosulphate with the values of the stability constants which were taken as ligands are presented in Table 2. The initial values of ion concentrations in the working solution are shown in Table 3.

Table 1

The values of the constants used to calculate the formation of HgSe and HgO

Variable	Value	Reference
pSP_{HgSe}	59.0	[10]
$pSP_{Hg(OH)_2}$	25.52	[10]
$pK^1_{HSe^-}$	3.89	[11]
$pK^2_{Se^{2-}}$	11.0	[11]
$pK^{1,2}_{H_2Se}$	14.89	[11,12]
$pK_{SeSO_3^{2-}}$	30.75	[12]

Table 2

The values of the instability constants of the selected complexes of Hg^{2+} ions [10]

L	pK^1_L	$pK^{1,2}_L$	$pK^{1,2,3}_L$	$pK^{1,2,3,4}_L$
SCN^-	–	17.60	20.40	21.20
I^-	12.87	23.82	27.60	29.83
$S_2O_3^{2-}$	–	29.86	32.36	33.61

Table 3

The values of the concentration used to calculate the formation of HgSe and HgO

Ion	Concentration
$[Hg^{2+}]$	0.01
$[SCN^-]$	1.0
$[I^-]$	0.04
$[S_2O_3^{2-}]$	0.5
$[SeSO_3^{2-}]$	0.01

As follows from Fig. 1, when potassium thiocyanate and potassium iodide are used as complexing agents, the precipitation of HgSe can occur throughout the whole pH range; it starts from pH >2.5 when thiosulphate is used.

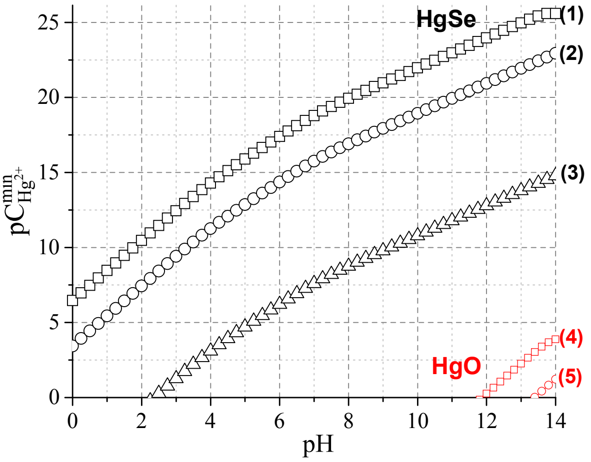

Fig. 1. The boundary conditions of the formation of HgSe and HgO in the Hg^{2+} – L_x – Na_2SeSO_3 system, where L_x is potassium thiocyanate (areas bounded by curves 1 and 4), potassium iodide (areas bounded by curves 2 and 5) or sodium thiosulfate (area bounded by curve 3), respectively

Table 4 shows the measured values of the pH values of the working solutions. It can be seen from obtained data that the pH value somewhat decreases during deposition. Obviously, the change in pH is affected by the decomposition of sodium selenosulfate, and by the differences in the composition of working solutions. When comparing the pH of the working solutions at the beginning of the synthesis and the data shown in Fig. 1, one can see that the formation of HgSe should begin at a concentration of the initial mercury salt of more than $1\cdot10^{-21}$ M when using potassium thiocyanate; if potassium iodide and thiosulphate were uses, this value is more than $1\cdot10^{-18}$ M and $1\cdot10^{-9}$ M, respectivly. The formation of a by-product, mercury oxide, in working solutions should not occur, since it begins only at pH >12.0 when using KSCN and at pH>13.5 when using KI.

Table 4

pH of working solutions in the synthesis of HgSe films with various complexing agents

Complexing agent	pH at the beginning of the synthesis	pH at the end of the synthesis
KSCN	9.2	8.0
KI	9.8	8.6
$Na_2S_2O_3$	8.6	8.4

In practice, it was not possible to obtain coatings at the minimum calculated concentrations. The minimum concentration of the initial mercury salt for the deposition of continuous and uniform HgSe thin films was $1 \cdot 10^{-2}$ M. Reducing the concentration significantly increased the deposition time, which was unpractical.

When the deposition process was completed, the surface of the substrates was completely covered with homogeneous HgSe films. In the case of using sodium thiosulphate, the largest amount of mercury selenide was mainly formed in the form of a film on the substrates surfaces and the walls of the bath and the formation of sediment was insignificant. When using potassium iodide, the amount of HgSe precipitate was higher. The use of potassium thiocyanate led to the formation of HgSe mainly in the form of a precipitate, the formation in the form of films was insignificant.

The phase composition of the synthesized samples was determined by the X-ray diffraction analysis (Fig. 2). From the obtained data, we found that in all cases the films are single-phase and consist of HgSe compound in cubic modification (structural type ZnS, sphalerite). The parameters of the HgSe cells with various complexing agents were as follows: a=0.60550(11) nm (when using KSCN), a=0.60523(16) nm (when using KI) and a=0.60834(10) nm (when using $Na_2S_2O_3$).

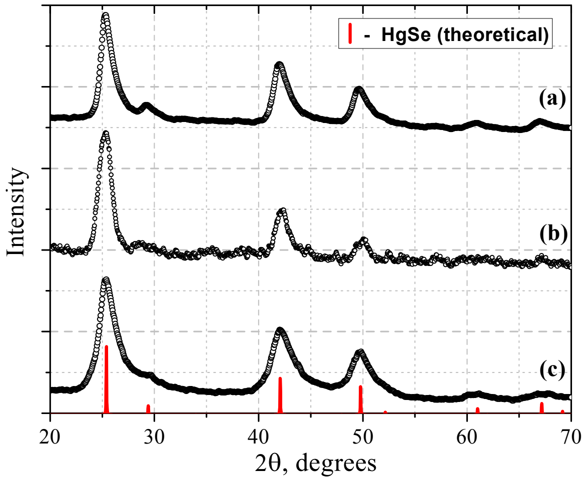

Fig. 2. The experimental profiles of diffractograms of HgSe films synthesized by using various complexing agents: potassium thiocyanate (a), potassium iodide (b) and sodium thiosulfate (c)

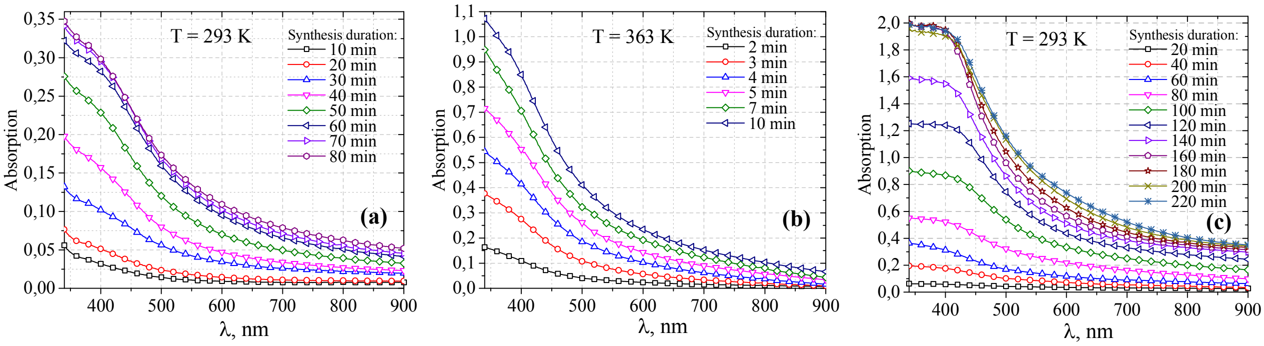

Fig. 3. Spectral dependences of optical absorption of HgSe films deposited on glass substrates using various complexing agents: potassium thiocyanate (a), potassium iodide (b) and sodium thiosulfate (c) at different synthesis durations

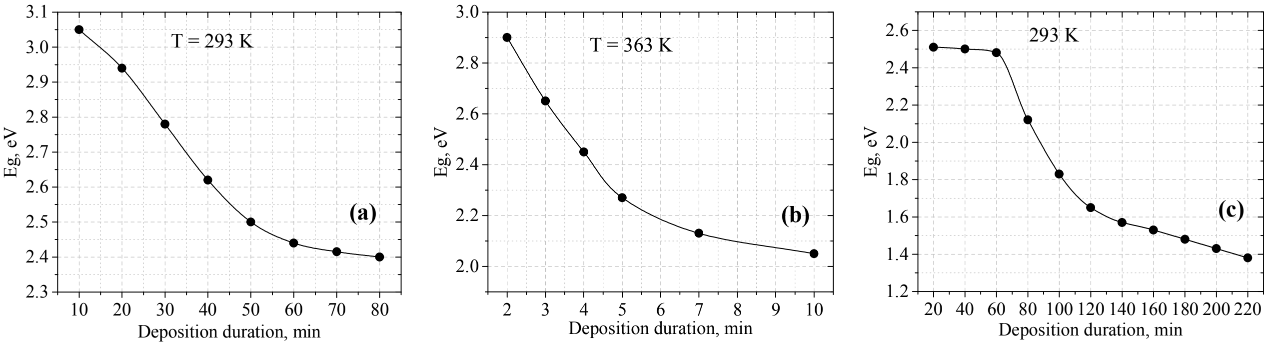

Fig. 4. Optical band gap band of HgSe films obtained using various complexing agents: potassium thiocyanate (a), potassium iodide (b), sodium thiosulfate (c) at different synthesis durations

The study of the optical properties of HgSe films (Fig. 3) revealed that they absorb more light waves as the duration of the synthesis increases; it is due to an increase of the HgSe amount in the films. In the ~400 nm region of wavelengths, the spectra showed a decrease in absorption. The maximum absorption (A) for all films was observed at the smallest investigated wavelength (340 nm). In the case of thiosulfate, HgSe films gave A=2.0, which was the best result. Almost twice less absorption was observed with potassium iodide (A=1.07) and the most less was found with potassium thiocyanate (A=0.35).

The optical band gap (E_g) numerically decreases with increasing the synthesis duration (Fig. 4). When using KSCN, E_g varies from 3.05 to 2.40 eV, and it is from 2.90 to 2.05 eV when using KI. When using $Na_2S_2O_3$, the range of E_g variation is the widest: from 2.52 to 1.38 eV. A larger value of absorption and a smaller of optical band gap of the samples mean a larger amount of deposited HgSe film on the substrate.

The investigation of the surface morphology of samples (Figs. 5–7) showed that HgSe films deposited by using KI and $Na_2S_2O_3$ are solid and homogeneous over the whole area with a small number of surface defects. The HgSe films obtained by using KSCN consist of spherical particles, the number and size of which increase with the duration of the synthesis. This explains the absence of a mirror hue of these films.

According to the results of microanalysis (Fig. 8), HgSe films are practically stoichiometric in their composition. The films have an insignificant excess of mercury atoms when using KI, and they have a slight excess of selenium atoms when using

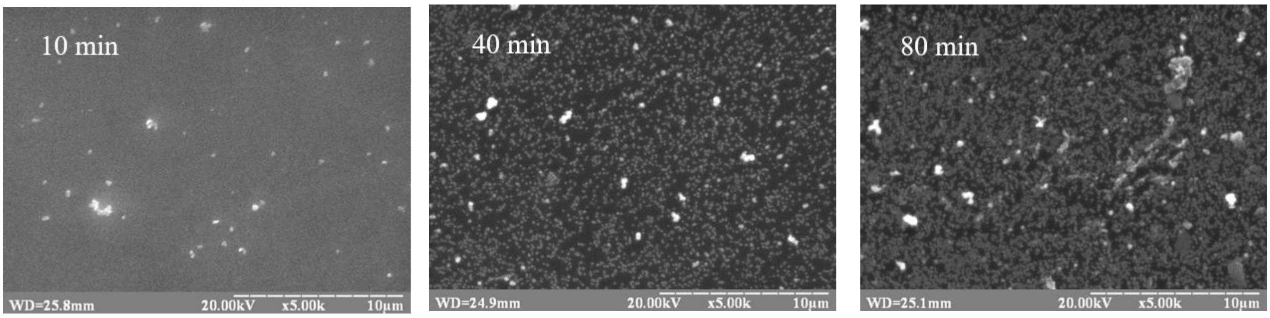

Fig. 5. Surface morphology of HgSe films obtained using KSCN at different deposition duration

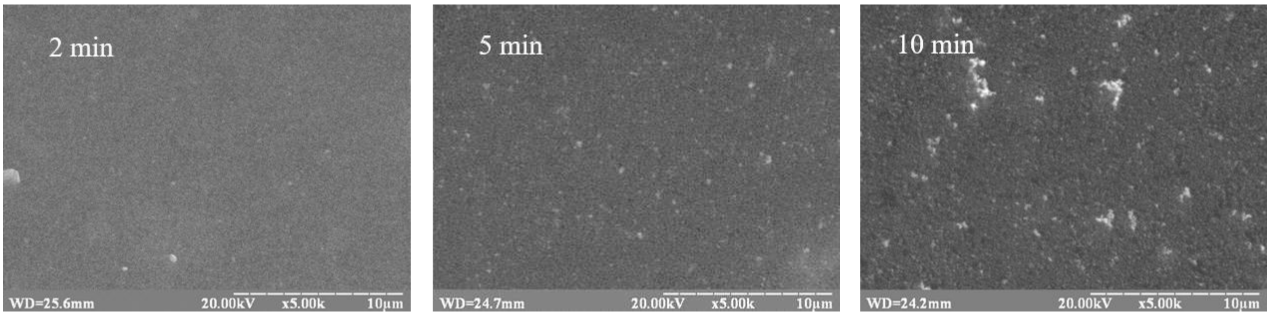

Fig. 6. Surface morphology of HgSe films obtained using KI at different deposition duration

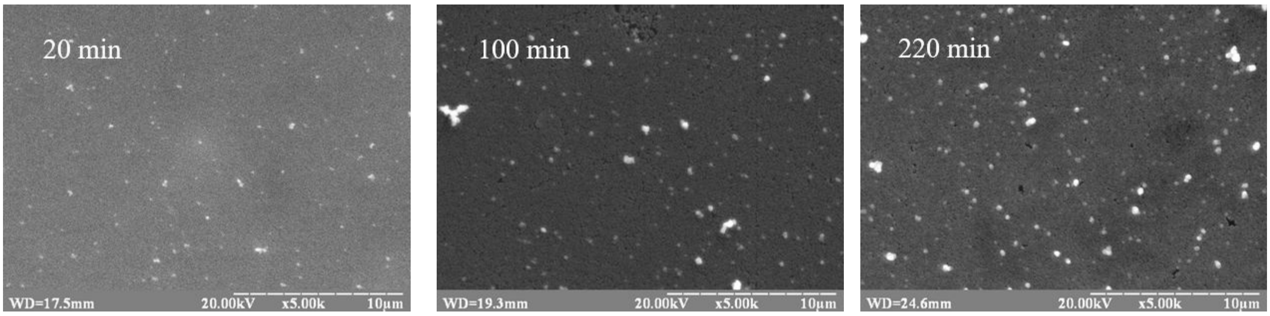

Fig. 7. Surface morphology of HgSe films obtained using $Na_2S_2O_3$ at different deposition duration

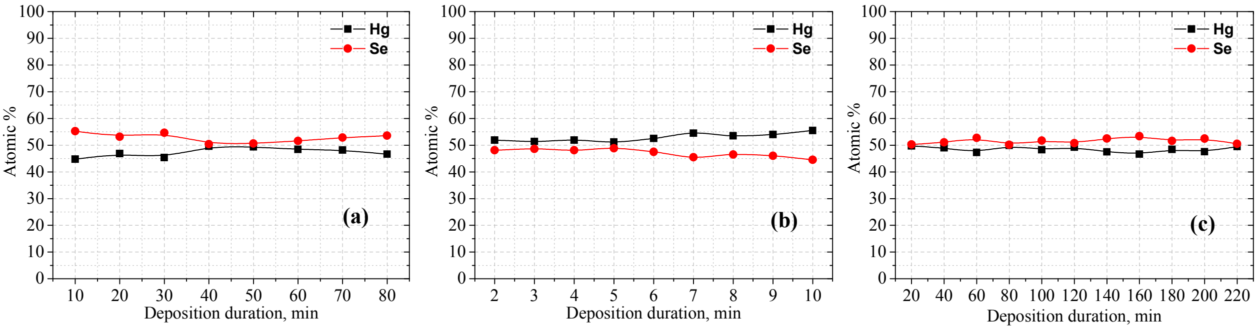

Fig. 8. The atomic composition of HgSe films, obtained by using different complexing agents: potassium thiocyanate (a), potassium iodide (b), sodium thiosulfate (c) at different deposition durations

KSCN and $Na_2S_2O_3$.

Conclusions

In this work, an attempt was made to comprehensively consider the synthesis of mercury selenide films in order to develop general rules and approaches for controlling the process of their hydrochemical synthesis. It has been established that the single-phase HgSe films were formed when using three different complexing agents: KSCN, KI and $Na_2S_2O_3$. The effect of these complexing agents on the optical, morphological properties of HgSe films and their atomic composition was studied. It is advisable to use sodium thiosulfate for the synthesis of HgSe films from an aqueous solution, because the films synthesized under such conditions are stoichiometric in composition, homogeneous, solid and have a mirror hue. Their optical absorption is the highest and it is possible to regulate the optical band gap in the widest range. The use of KI for the synthesis of HgSe films also gives good results, but here it is necessary to use a high synthesis temperature (363 K) instead of room temperature. Therefore, there is a need for additional expenditure of energy. The deposition of mercury selenide films with KSCN solutions is inadvisable due to the absence of a mirror hue, small optical absorption of the films, and the formation of HgSe mainly as a precipitate.

Acknowledgments

This research was conducted in the framework of the project «Thin film semiconductor materials for photo sensitive solar cells» (No. 0117U004455).

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Received 05.02.2018

ВПЛИВ РІЗНИХ КОМПЛЕКСОУТВОРЮЮЧИХ РЕАГЕНТІВ НА СТРУКТУРУ І ВЛАСТИВОСТІ ПЛІВОК МЕРКУРІЙ СЕЛЕНІДУ, ОСАДЖЕНИХ З ВОДНИХ РОЗЧИНІВ

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Методом гідрохімічного осадження з ванн одержано плівки меркурій селеніду (HgSe) на скляних підкладках з використанням водних розчинів меркурій (II) нітрату, натрій селеносульфату і комплексоутворюючого реагенту (калій роданіду, калій йодиду або натрій тісульфату). Було здійснено комплексні дослідження, які включають: теоретичний розрахунок граничних умов утворення меркурій селеніду і меркурій оксиду з різними лігандами, екпериментальне дослідження складу, структури, оптики і морфології синтезованих напівпровідникових плівок HgSe в залежності від впливу трьох різних комплексоутворюючих реагентів. Одержані плівки є однофазні, сфалеритної структури. Вони мають однорідну суцільну поверхню, практично стехіометричний склад і широкий інтервал зміни оптичної ширини забороненої зони. Аналіз отриманих експериментальних результатів дав змогу пов'язати умови осадження HgSe з властивостями одержаних напівпровідникових плівок, виявити переваги та недоліки використаних комплексоутворюючих реагентів, встановити доцільність їх використання.

Ключові слова: меркурій селенід, напівпровідникові плівки, хімічне осадження, оптичні властивості, аналіз морфології.

THE EFFECT OF DIFFERENT COMPLEXING AGENTS ON THE PROPERTIES OF MERCURY SELENIDE FILMS DEPOSITED FROM AQUEOUS SOLUTIONS

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The mercury selenide (HgSe) films were obtained on glass substrates by chemical bath deposition method with using aqueous solutions of mercury (II) nitrate, sodium selenosulfate and complexing agents (potassium thiocyanate, potassium iodide or sodium thiosulfate). In this work, the complex studies were performed, including the theoretical calculation of boundary conditions for the formation of mercury selenide and mercury oxide with various ligands, and the experimental investigation of the composition, structure, optics and morphology of the synthesized HgSe semiconductor films, depending on the effect of three different complexing agents. The obtained films are single-phase and have a sphalerite structure. They have a homogeneous solid surface with the practically stoichiometric composition and a wide interval of the variation of optical band gap. An analysis of the obtained experimental results allows relating the HgSe deposition conditions to the properties of the obtained semiconductor films, revealing the advantages and disadvantages of the used complexing agents and determining the expediency of their use.

Keywords: mercury selenide; semiconductor films; chemical deposition; optical properties; morphology analysis.

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