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OPTIMIZATION OF SYNTHESIS CONDITIONS OF HgS THIN FILMS

**M. Sozanskyi*, V. Stadnik, R. Guminilovych,
P. Shapoval, M. Laruk, Yo. Yatchyshyn**

*Lviv Polytechnic National University,
S. Bandera Str., 12, 79013 Lviv, Ukraine
e-mail: martyn.a.sozanskyi@lpnu.ua*

The mercury sulfide (HgS) films were obtained on glass substrates via the chemical deposition method. The aqueous solutions of mercury(II) nitrate, thiourea and trisodium citrate were used. X-ray and elemental analysis of the film sample were made. The effect of concentrations of initial reagents, deposition duration and temperature on the mass of HgS coatings was investigated and their thickness were calculated. The optical and morphological properties of HgS coating were examined.

Keywords: mercury sulfide, thin films, chemical deposition, optical properties.

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The mercury sulfide (HgS) film is one of the least investigated material of zinc subgroup metal chalcogenides [1]. The HgS coatings have potential use in solid state solar cells, photoelectrochemical cells etc. The one of the simplest methods for semiconductor films obtaining is chemical deposition [2]. This method based on synthesis at low temperature (< 373 K) and duration from aqueous solutions, which consist of the metal salt, complexing agent, chalcogenizer and, if it's necessary, the pH-regulator. Previously, the anodic stripping voltammetry method was used for the optimization of these parameters for synthesis of zinc and cadmium chalcogenides semiconductor films [3–5]. The series of films samples had dissolved in hydrochloric acid, then the measurements of metal content were made. In the case of mercury, this is difficult to apply, so the optimization of chemical deposition of HgS films could be done by gravimetric measurements.

Chemical deposition of HgS films was carried out on preliminarily cleaned square shape glass substrates with the total area of 64.8 cm². The composition of the working solutions were follows: 0.0025 – 0.015 M of mercury(II) nitrate ($\text{Hg}(\text{NO}_3)_2$), 0.01 – 0.05 M of thiourea ($(\text{NH}_2)_2\text{CS}$), as a complexing and chalcogenizing agent for Hg^{2+} at the same time; and 0.015 – 0.021 M of trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), as a pH regulator. The deposition was made in a glass bath during 0.5 – 7 minutes at a temperature of 323 – 363 K. After this, the substrates were removed, washed with distilled water and dried in the air. The films samples were dark-brown in color. Their adhesion to the glass substrate was weak. The films were easily removed at applying of small mechanical efforts.

Experimental arrays of intensities and angles of reflection of the test samples were obtained on a DRON-3.0 X-ray diffractometer (CuK_α -radiation). Preliminary processing of the experimental diffraction arrays in order to identify the phases were carried out using PowderCell program [6].

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

Investigation of the films surface morphology were performed on Atomic Force Microscope (AFM) MultiMode Nanoscope IIIa (Bruker) in tapping mode using Super Sharp Silicon tips SSS-NCLR (Nanosensors) with typical spring constant $k=33$ N/m and resonance frequency about 180 kHz.

Elemental analysis of film was carried out on an X-ray fluorescence (XRF) spectrometer ElvaX Light SDD (Elvatech).

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

In order to optimize the deposition process, the gravimetric measurements were carried out. The mass of deposited HgS films were recalculated to the unit of the substrate square. For this purpose, the differences of substrates mass before and after deposition has been measured and the differences in mass were established. The weighing of the samples were carried out on with the use of Radwag AS 220.R2 analytical weight (accuracy – 0.0002 g) depending on the concentrations of initial reagents in the working solution, the duration and temperature of deposition.

To conduct the research on optimization of Hg-containing salt initial concentration the working solutions were prepared with 0.02 M thiourea and 0.015 M trisodium citrate. Concentration of $\text{Hg}(\text{NO}_3)_2$ varied from 0.0025 to 0.015 M. The temperature of process was 363 K. The deposition duration was 5 minutes.

To conduct the research of optimization of initial concentration of thiourea, the working solutions were prepared with 0.01 M mercury(II) nitrate and 0.15 M trisodium citrate. Concentration of $(\text{NH}_2)_2\text{CS}$ was varied from 0.01 to 0.05 M. The temperature of process was 363 K. The deposition duration was 5 minutes.

To conduct the research of optimization of initial concentration of trisodium citrate, the working solutions were prepared with 0.01 M mercury(II) nitrate and 0.04 M thiourea. Concentration of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ was varied from 0.0015 to 0.021 M. The temperature of process was 363 K. The deposition duration was 5 minutes.

To conduct the research on optimization of deposition time, the working solutions were prepared with 0.01 M mercury(II) nitrate, 0.04 M thiourea and 0.015 M trisodium citrate. The temperature of process was 363 K. The deposition duration varied from 0.5 to 7 minutes.

To conduct the research on optimization of deposition temperature the working solutions were prepared with 0.01 M mercury(II) nitrate, 0.04 M thiourea and 0.015 M trisodium citrate. The deposition duration was 5 minutes. The temperature of process varied from 323 K to 363 K.

The calculation of HgS films thickness according to the measured mass of coatings were carried out based on the following considerations:

1. The volume of the deposited film on the substrate equal:

$$V = \frac{\Delta m}{\rho} = \frac{m_2 - m_1}{\rho} \quad [cm^3], \quad (1)$$

where Δm is the film mass, g; m_1 is the mass of substrate before synthesis, g; m_2 is the mass of substrate after synthesis, g; ρ is the compound density, g/cm^3 ($8.10 g/cm^3$ for HgS).

2. Since the synthesis were performed on substrates with the square shape, it is possible to assume that the coatings had approximately the shape of the parallelepiped and the volume of the film is:

$$V = S \cdot d \quad [cm^3], \quad (2)$$

where S is the substrate surface square, cm^2 , d is the height (thickness) of the film, cm .

3. Equating (1) and (2) we can derive a formula for calculating the average thickness of HgS films from the mass of coating:

$$d = \frac{m_2 - m_1}{S \cdot \rho} \quad [cm]. \quad (3)$$

In nanometre size (which is more convenient for thin films) and considering that the film is deposited on both sides of the substrate it can be presented as follows:

$$d = \frac{m_2 - m_1}{2a^2 \cdot \rho} \cdot 10^{-7} \quad [nm], \quad (4)$$

where a – is length of the substrate side.

By measuring of the deposited HgS films mass, the dependences of its changes on the synthesis conditions were constructed. According to equation (4), the films thicknesses were calculated. The research results are presented in Fig. 1 and Fig. 2.

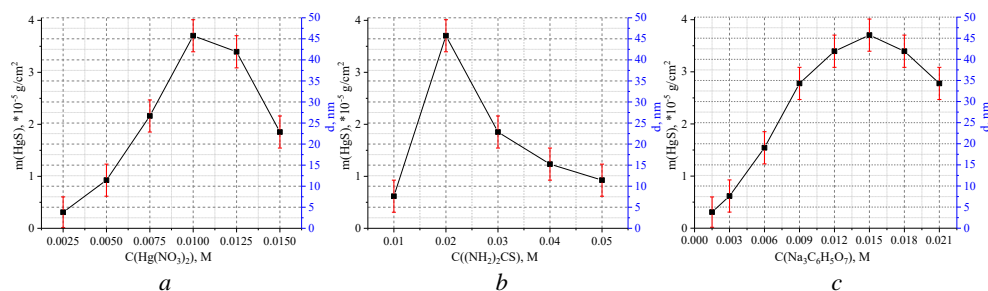


Fig. 1. Dependences of the HgS mass changes per unit of substrate surface area on the concentration of: *a* – Hg-containing salt; *b* – $(NH_2)_2CS$; *c* – $Na_3C_6H_5O_7$

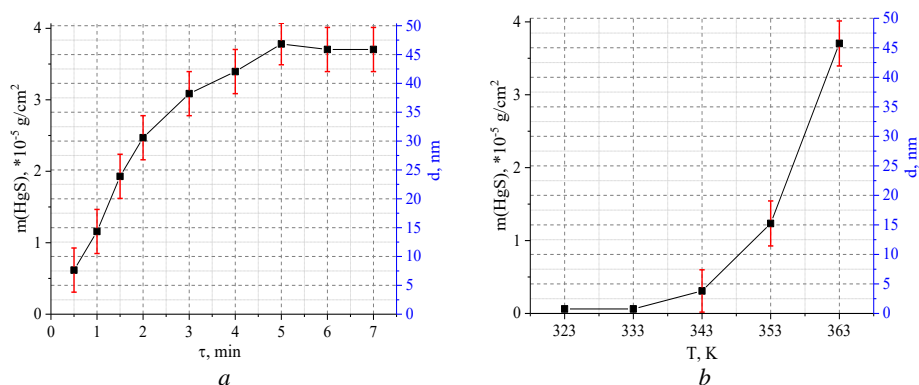


Fig. 2. Dependences of the HgS mass changes per unit of substrate surface area on: *a* – deposition duration; *b* – temperature of synthesis

From the obtained data (Fig. 1, *a*), it is seen that at $C(\text{Hg}(\text{NO}_3)_2) \leq 0.01$ M the plot is close to linear. At $C(\text{Hg}(\text{NO}_3)_2) > 0.01$ M, the mercury sulfide was partially precipitated before the addition of the last component of trisodium citrate. In this case, the amount of mercury(II) ions in the solution, necessary for the formation of the film, is reduced. This is because a ratio of thiourea to mercury salt is less than 2 to 1 (more details about the features of such ratios are described below). Thus, the optimized value of mercury salt concentration is 0.01 M.

The mass change of HgS films, deposited at various concentrations of thiourea (Fig. 1, *b*) has an extremum character dependence. At $C(\text{NH}_2)_2\text{CS} = 0.01$ M, the ratio of thiourea to the mercury salt is 1 : 1. When these reagents was mixed in such proportions, a precipitate of brown-black in colour begins to fall, as in the previous case. Also, sometimes there was a slight white turbidity, probably due to the partial formation of mercury oxide. This may indicate a fairly small stability of one-coordinated complex of mercury with thiourea. The amount of deposited mercury sulfide on the substrates from remaining Hg ions in the solution at addition of trisodium citrate were small. At $C((\text{NH}_2)_2\text{CS}) = 0.02$ M, the ratio of thiourea to mercury salt is 2 : 1. In this case, the solution has a saturated dark brown in colour without precipitation. The mass of deposited HgS film on the substrate is maximal after $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ adding to it. At $C((\text{NH}_2)_2\text{CS}) \geq 0.03$ M, the working solution turns brown at a much lower intensity than in the previous case. At this, the mass of HgS film is much lower due to the formation of more coordinated and more stable complex with mercury with thiourea. Thus, the optimized value of thiourea concentration is 0.02 M.

An increase of the concentration of trisodium citrate (Fig. 1, *c*) in the range of 0.0015–0.015 M leads to a practically linear increase of the HgS films mass. In this case, the pH of the working solution varies from 5.74 to 7.01 (Table 1). Further growth of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ concentration in the working solution over 0.015 M leads to the increase the rate of HgS formation in the form of precipitate and not as a film. The hydrogen index goes into the alkaline area. It explains the decrease of the mass of HgS films in this area. Thus, the optimized value of trisodium citrate concentration is 0.015 M.

With the increase of deposition duration (Fig. 2, *a*), the mass of HgS films increases linearly in the time interval of 0.5–2 minutes. Within 2–5 minutes the mass gain decreases and after 5 minutes of synthesis, the HgS films mass practically didn't change. Thus, the optimized value of the deposition time is 5 minutes.

In the study of the temperature influence on the HgS films synthesis (Fig. 2, *b*), it can be seen that at the temperatures of 323 K and 333 K, the coatings on glass substrates were practically absent. The largest mass of HgS film was observed at 363 K. Reducing the temperature significantly reduces the amount of deposited HgS film. Thus, the optimized temperature is 363 K.

From the studies above, the optimized conditions for HgS films deposition are following: the concentrations of mercury salt, thiourea and trisodium citrate in the working solution is 0.01 M, 0.02 M, 0.015 M, respectively; deposition duration – 5 minutes and temperature – 363 K. At these conditions the greatest average thickness of HgS film was reached and equal to 46 nm.

The X-ray phase analysis (Fig. 3) of HgS film was performed. It was established that the coating is single-phase and contain HgS in the trigonal modification (HgS structure type).

Table 1

The measured pH values of the working solutions after adding various quantities of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$

$\text{C}(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7)$, M	The pH of the solution, which contained:		
	0.01 M $\text{Hg}(\text{NO}_3)_2$ + 0.02 M $(\text{NH}_2)_2\text{CS}$	0.01 M $\text{Hg}(\text{NO}_3)_2$ + 0.02 M $(\text{NH}_2)_2\text{CS}$ + $\text{C}(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7)$ (at the start of deposition)	0.01 M $\text{Hg}(\text{NO}_3)_2$ + 0.02 M $(\text{NH}_2)_2\text{CS}$ + $\text{C}(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7)$ (at the end of deposition)
0.0015	3.24	5.74	5.86
0.003		6.17	6.17
0.006		6.55	6.45
0.009		6.78	6.57
0.012		6.92	6.65
0.015		7.01	6.69
0.018		7.08	6.73
0.021		7.12	6.75

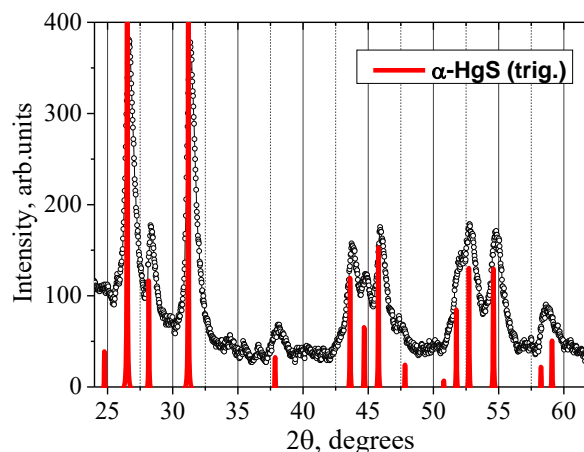


Fig. 3. The X-ray diffraction pattern of HgS film, obtained at optimized conditions and its comparison with the lines of theoretical diffraction pattern of HgS

The optical transmission spectra $T(\lambda)$ (Fig. 4, *a*) of HgS films, obtained at different deposition duration (other synthesis parameters were equal to the optimized ones). The minimum light transmission (T_{\min}) in the investigated range located at wavelength of 340 nm. An increase of the light transmission can be seen at greater wavelengths. The maximum light transmission (T_{\max}) in the investigated range located at wavelength of 900 nm. In the range of deposition duration of 0.5–5 min T_{\min} and T_{\max} decreases from ~ 48 % to 18 % and from ~ 85 % to 72 %, respectively. Absorption spectra dependences in $(\alpha \cdot hv)^2 = f(hv)$ coordinates of HgS films (Fig. 4, *b*) show the presence of the fundamental optical absorption edge. The optical band gaps (defined as the intersection point of the tangent to linear section of the dependence $(\alpha \cdot hv)^2 = f(hv)$ and the x-axis) decreases numerically from 3.20 to 2.84 eV at deposition duration of 0.5–5 min. This is due to thickness increase during the growth of the coatings. The obtained values of optical band gaps are close to the works of authors [7–8].

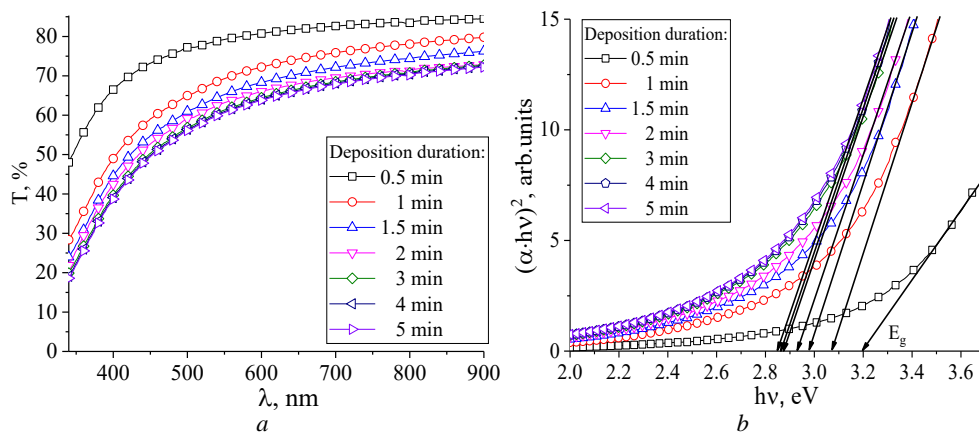


Fig. 4. Spectral dependences of optical transmission (T , %) (*a*) and dependence $(\alpha \cdot hv)^2 = f(hv)$ (*b*) of HgS films (where α – optical absorption coefficient)

AFM studies of the surface morphology (Fig. 5) of HgS film, obtained at optimized conditions, showed that coating is solid and homogeneous. It consists of particles with the irregular shape. Their average height is close to 50 nm, which corresponds to the calculated value by mass measurement of the film.

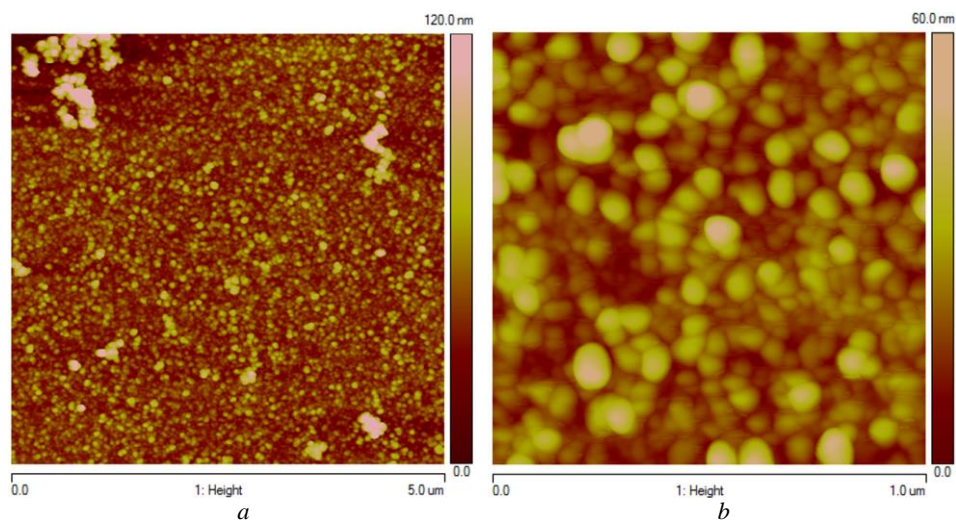


Fig. 5. AFM images of $5 \times 5 \mu\text{m}$ (*a*) and $1 \times 1 \mu\text{m}$ size (*b*) of HgS film, obtained at optimized conditions

According to the results of elemental analysis (Fig. 6), the HgS films have a practically stoichiometric composition with a slight excess of sulfur atoms.

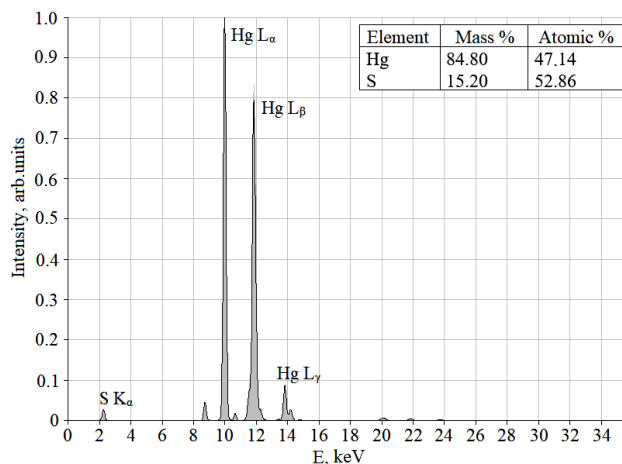


Fig. 6. X-ray fluorescence spectrum and results of elemental analysis of HgS film

So, this work shows the possibility of using the chemical deposition method for the synthesis of single-phase HgS films with using thiourea as complexing and chalcogenizing agent at the same time. By changing the process parameters, the conditions were found under which mercury sulfide deposit predominantly in the form of a coating and not as a precipitate. Thus, the conditions of films obtaining were optimized. It was found that HgS films obtained in this way are not inferior in their characteristics to the same films, obtained by other methods [9–12] and can be used in photosensitive applications.

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ОПТИМІЗАЦІЯ УМОВ СИНТЕЗУ ТОНКИХ ПЛІВОК HgS

**М. Созанський*, В. Стаднік, Р. Гумінілович, П. Шаповал, М. Ларук,
Й. Ятчишин**

*Національний університет “Львівська політехніка”,
вул. С. Бандери, 12, 79013 Львів, Україна,
e-mail: martyn.a.sozanskyi@lpnu.ua*

Методом хімічного осадження отримано плівки ртутної сульфідної на скляних підкладах. Для цього використано свіжоприготовані розчини ртутної(II) нітрату, тіосечовини та тринатрій цитрату. Тіосечовина виконувала роль одночасно комплексуютьовального та халькогенізуючого реагента, а тринатрій цитрат – регулятора рН середовища. Проведеним рентгенофазовим аналізом підтверджено, що плівки є однофазними та містять HgS в тригональній модифікації (структурний тип HgS). Для оптимізації процесу синтезу проведено гравіметричне визначення маси осадженої плівки HgS. Для цього брали різницю мас-підкладок до і після осадження залежно від концентрації початкових реагентів у робочому розчині, тривалості та температури осадження. На основі отриманих результатів розраховано товщину плівок HgS. За зміни параметрів процесу визначено їхні оптимізовані значення, за яких HgS осідав переважно у вигляді покриття, а не осаду. На основі отриманих даних з'ясовано, що оптимізованими умовами синтезу плівок HgS є такі концентрації солі ртутної(II), тіосечовини та тринатрій цитрату у робочому розчині: 0,01 М; 0,02 М;

0,015 M, відповідно; час осадження – 5 хв і температура – 363 K. При цьому середовище робочого розчину є близьким до нейтрального. За таких умов досягнуто найбільшу середню товщину плівок HgS, яка становила 46 нм. Визначено спектри оптичного пропускання $T(\lambda)$ (при $\lambda = 340\text{--}900$ нм) для плівок HgS, отриманих за різних тривалостей синтезу (інші параметри синтезу дорівнюють оптимізованим). Мінімальне пропускання (T_{\min}) в досліджуваному діапазоні λ є за довжини хвилі 340 нм. За більших довжин простежується стрибок, який виходить на максимальне пропускання (T_{\max}) при $\lambda = 900$ нм. У діапазоні тривалостей синтезу 0,5–5 хв T_{\min} та T_{\max} зменшуються від ~ 48 до 18 % та від ~ 85 до 72 %, відповідно. Отже, оптична ширина забороненої зони плівки HgS чисельно зменшується з 3,20 до 2,84 eV, що пов'язано зі збільшенням товщини під час росту покриття. Дослідження морфології поверхні плівки HgS, отриманої в оптимізованих умовах, показали, що покриття є суцільним та однорідним. Його поверхня складається з частинок неправильної форми. Їхня середня висота близька до 50 нм, що відповідає розрахованій величині за масою покриття. Згідно з результатами елементного аналізу, плівка HgS має практично стехіометричний склад з невеликим надлишком атомів сірки (Hg : S = 47,14 : 52,83). Проведені дослідження підтвердили високу ефективність використання методу хімічного осадження для виготовлення плівок HgS.

Ключові слова: меркурій сульфід, тонкі плівки, хімічне осадження, оптичні властивості.

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