CHEMISTRY. CHEMICAL ENGINEERING

ХІМІЯ. ХІМТЕХНОЛОГІЯ

UDC 539.232

M.A. Sozanskyi[1], Master,
P.I. Shapoval[1], PhD, Assoc.Prof.,
I.I. Yatchyshyn[1], DSc, Prof.,
V.E. Stadnik[2], Master,
R.E. Gladyshevskii[2], DSc, Prof., Corresponding Member of the NAS of Ukraine
[1] Lviv Polytechnic National University, 12 Bandera Str., 79013 Lviv, Ukraine; e-mail: sozanskyi.m@gmail.com
[2] Ivan Franko National University of Lviv, 1 Universytetska Str., 79000 Lviv, Ukraine

SYNTHESIS OF ZnS THIN FILMS FROM AQUEOUS CAUSTIC OF TRISODIUM CITRATE AND THEIR PROPERTIES

М.А. Созанський, *П.Й. Шаповал*, *Й.Й. Ятчишин*, *В.Є. Стаднік*, *Р.Є. Гладишевський*. **Синтез тонких плівок ZnS з водного розчину тринатрій цитрату та їх властивості.** Тонкі плівки цинк сульфіду (ZnS) завдяки своїм властивостям широко застосовуються в різних оптичних електронних пристроях. Їх отримують різними методами, серед яких – вакуумна сублімація, високочастотне розпилення, метод квазізамкнутого об'єму, золь-гелевий метод, електроосадження. Перелічені методи мають високу енергозатратність, що збільшує ціну тонких плівок ZnS. ***Мета:*** Метою роботи є встановлення оптимальних умов синтезу тонких плівок ZnS з водного розчину та взаємозв'язку між вмістом цинку в синтезованих плівках, визначеного за допомогою методу інверсійної вольтамперометрії, з їхньою товщиною, структурними, оптичними та морфологічними параметрами. ***Матеріали і методи:*** Тонкі плівки ZnS отримано із водних розчинів цинк-вмісної солі методом хімічного осадження. Для синтезу плівок цинк сульфіду використовували свіжоприготовані розчини цинк-вмісної солі, тринатрійцитрату ($Na_3C_6H_5O_7$) як комплексоутворювача, тіосечовини ($(NH_2)_2CS$) і амоній гідроксиду (NH_4OH). Осадження проводили на попередньо підготовані скляні підкладки площею 5,76 см^2. ***Результати:*** Встановлений фазовий склад плівок, який показав наявність сполуки ZnS в кубічній модифікації (сфалерит). Методом інверсійної вольтамперометрії визначено масу цинку в плівках ZnS від різних умов синтезу, а саме від концентрації вихідної цинк-вмісної солі, тринатрій цитрату, тіосечовини, часу осадження і температури. Досліджено морфологію поверхні, оптичні властивості, товщину отриманих плівок цинк сульфіду. ***Висновки:*** На основі отриманих даних встановлені оптимальні умови синтезу плівок ZnS. Тривимірні дослідження морфології поверхні плівки ZnS показало її гладкість, однорідність, суцільність і підтвердило правильність визначення оптимальних параметрів синтезу.
Ключові слова: тонкі плівки ZnS, інверсійна вольтамперометрія, хімічне осадження.

M.A. Sozanskyi, *P.I. Shapoval*, *I.I. Yatchyshyn*, *V.E. Stadnik*, *R.E. Gladyshevskii*. **Synthesis of ZnS thin films from aqueous caustic of trisodium citrate and their properties.** Zinc sulfide (ZnS) thin films due to their properties are widely used in various electronic optical devices. They are produced by several methods, among which – vacuum sublimation, high frequency sputtering method, quasiclosed volume method, sol-gel method, electrodeposition. These methods have high energy consumption which increases the price of ZnS thin films. ***Aim:*** The aim of this work is to establish the optimal parameters of the synthesis of ZnS thin films of the aqueous caustic and the correlation between content of zinc in the synthesized films determined by the method of stripping voltammetry and thickness, structural, morphological and optical parameters. ***Materials and Methods:*** The ZnS thin films were obtained from aqueous caustics of zinc-containing salt using chemical deposition. Fresh solution of zinc-containing salt, trisodium citrate ($Na_3C_6H_5O_7$) as a complexing agent, thiourea ($(NH_2)_2CS$) and ammonium hydroxide (NH_4OH) was used for the synthesis of ZnS films by chemical deposition. The deposition was performed on prepared glass substrates with the area of 5,76 cm^2. ***Results:*** The phase mixture of the films has been determined. It showed the presence of ZnS compounds in the cubic modification (sphalerite). Stripping voltammetry was used to determine the mass of zinc in the ZnS films on various conditions of synthesis, namely on the concentration of the initial zinc-containing salt, trisodium citrate, thiourea, deposition time and temperature. The surface morphology, optical properties, the thickness of the ZnS resulting films have been studied. ***Conclusions:*** The optimal conditions for the synthesis of ZnS films were found based on these data. Three-dimensional surface morphology of ZnS film studies showed its smoothness, uniformity, integrity and confirmed the correctness of determining the optimal synthesis parameters.
Keywords: ZnS thin films, stripping voltammetry, chemical deposition.

Introduction. Thin films of zinc sulfide (ZnS) due to their properties are widely used in various

DOI 10.15276/opu.3.47.2015.17

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

electronic optical devices. They are produced by several methods, among which — vacuum sublimation, high frequency sputtering method, quasiclosed volume method, sol-gel method, electrodeposition. These methods have high energy consumption which increases the price of ZnS thin films. To reduce the cost of manufacturing process the chemical deposition method can be used. Firstly, his can ensure obtaining of thin films of zinc sulfide which characteristics are not inferior to similar films produced by other methods. Secondly, there are no need to use complicated equipment and expensive reagents. Thirdly, it is easy to control the deposition process parameters that will allow comprehensive study the influence of synthesis conditions on the properties and produce films with the required structure, thickness, small amounts of surface defects and other properties required for practical use.

It is necessary to develop common rules that are bound the conditions of deposition with their properties for the controlled synthesis of ZnS thin films. The successful solution of the problem requires using of modern experimental research methods to study the composition, structure, surface morphology, that will determine the performance of ZnS thin films.

There are information in literature on the study of cadmium sulfide and cadmium selenide thin films using the method of stripping voltammetry [1, 2]. It has been shown that the stripping voltammetry can be used to measure the mass of cadmium in the CdS and CdSe films which has a direct relationship with the films thickness. That means from knowledge of the mass of metal in the films the thickness could be foreseen and this accelerates and simplifies the control of their synthesis process. Similarly, the mass of zinc in the ZnS films obtained under various conditions can be measured at analysers operating on basis of stripping voltammetry. Comparison of these data with the results of other researches should lead to the rational synthesis characterization of ZnS thin films and reducing the amount of source materials and waste.

The aim of the research is to establish the optimal parameters of the synthesis of ZnS thin films of the aqueous caustic and the correlation between content of zinc in the synthesized films determined by the method of stripping voltammetry and thickness, structural, morphological and optical parameters.

Materials and Methods. Fresh solution of zinc-containing salt, trisodium citrate ($Na_3C_6H_5O_7$) as a complexing agent, thiourea ($(NH_2)_2CS$) and ammonium hydroxide (NH_4OH) was used for the synthesis of zinc sulfide films by chemical deposition. The molar concentration of zinc-containing salt in the working solution was varied in the range of 0,01 to 0,05 M, trisodium citrate — 0,03 to 0,07 M, Thiourea — 0,025 to 0,25 M, the deposition time — from 40 to 120 minutes, the temperature – from 50 to 90 °C. To maintain pH $\geq$ 9,5 that required for a sufficient hydrolysis of thiourea in the deposition process there was added a small, constant amount of ammonium hydroxide (0,01 volume fraction of the total volume of working solution). The deposition was performed on prepared glass substrates with the area of 5,76 cm^2.

Arrays of experimental intensities and angles of reflection from the investigated samples were obtained on a DRON-3.0 (CuK α-radiation) diffractometer. Primary processing of the experimental diffraction array and calculation of the theoretical diffraction patterns of known compounds in order to identify the phases were performed using PowderCell software [3].

The optical properties of zinc sulfide films researches were held using Lambda 25 spectrophotometer (Perkin-Elmer). The surface morphology of ZnS films was investigated using raster electron microscope REM-106I with system of microanalysis. A comparative signal passed through the glass substrates identical to the investigated films substrates. Three-dimensional surface morphology of ZnS films is performed using an atomic force scanning probe microscope (AFM) Solver P47 PRO (NT-MDT) by semi-contact and contact methods (having scanning frequency 1 Hz) using silicon probe device NSG 10 A (the curvature radius of the fang is 10 nm). All studies were performed in air. The experimental data processing and the calculation of the surface morphology parameters were performed using the Image Analysis 2 software suite (NT-MDT).

The stripping voltammetry method was used to investigate the zinc content in the films (“Tomanalyt NVP” analyser). The ZnS films had been dissolved for this in a precise volume of 0,1 M hydrochloric acid solution and by method of additives the determination of content of Zn^{2+} ions was done via TALab 3.6 application.

The thickness of films was measured using DEKTAK IIA profile testing instrument (SLOAN).

The synthesized ZnS films were white colour on the surface of the glass substrates — typical colour for ZnS compound, and mirror reflexion that indicates uniformity of coating and good adhesion to the glass substrate.

The X-ray phase analysis of the samples of ZnS films where performed (Fig. 1). These films were received from various zinc salts (zinc chloride ($ZnCl_2$), zinc acetate ($(CH_3COO)_2Zn$), zinc nitrate ($Zn(NO_3)_2$), zinc sulfate ($ZnSO_4$)). It was found that in all cases of films formation they consist of the phase of ZnS compound in cubic modification (sphalerite). So, the nature of zinc-containing salt does not affect on crystalline structure of ZnS films. Therefore, in future synthesis of the films and their researches the zinc chloride had been used.

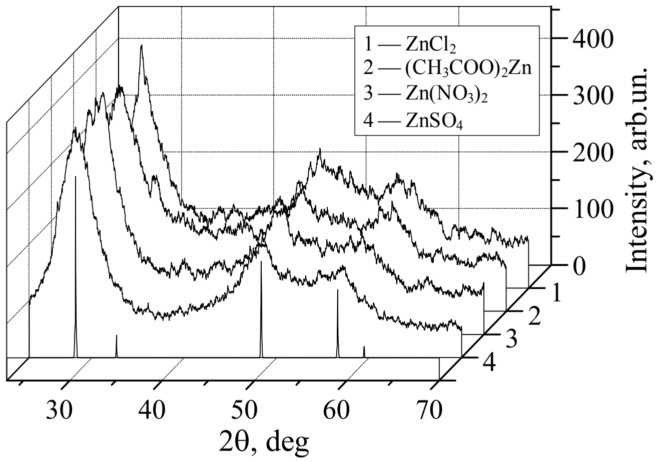

Fig. 1. The experimental profiles of diffraction patterns of ZnS films obtained from different zinc salts and their comparison with the lines of theoretical diffraction pattern of ZnS

To conduct the research on optimization of zinc-containing salt initial concentration the working solutions were prepared with 0,04 M trisodium citrate, 0,01 M thiourea. Concentration of zinc chloride varied from 0,01 to 0,05 M. The temperature of process was 70 °C. The deposition time was 80 minutes.

To conduct the research of optimization of initial concentration of trisodium citrate, the working solutions were prepared with 0,04 M zinc chloride, 0,10 M thiourea. Concentration of trisodium citrate was varied from 0,03 to 0,07 M. The temperature of process was 70 °C, The deposition time was 80 minutes.

To conduct the research of optimization of initial concentration of thiourea, the working solutions were prepared with 0,04 M zinc chloride, 0,04 M trisodium citrate. Concentration of thiourea was varied from 0,025 to 0,25 M. The temperature of process was 70 °C. The deposition time was 80 minutes.

To conduct the research on optimization of deposition temperature the working solution was prepared with 0,04 M zinc chloride, 0,04 M trisodium citrate, 0,10 M thiourea. The deposition time was 80 minutes. The temperature of process varied from 50 to 90 °C.

To conduct the research on optimization of deposition time, the working solutions were prepared with 0,04 M zinc chloride, 0,04 M trisodium citrate, 0,10 M thiourea. The temperature of process was 70 °C. The deposition time varied from 40 to 120 minutes.

Results. The research results are presented in Figures 2, 3.

The obtained data show the zinc weight of ZnS films increases linearly with the zinc salt strengthening. When concentration of $ZnCl_2$ in the working solution was 0,05 M the formation of precipitate of zinc hydroxide there were observed. This can be explained by the deficient amount of complexing agent of trisodium citrate (0,04 M) for binding of zinc ions in complex of zinc citrate ($Zn[C_6H_5O_7]^-$). Thus, the optimal value of the concentration of zinc salt is 0,04 M. This corresponds to a molar ratio of zinc salt to trisodium citrate as 1:1.

 ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

The mass of zinc in the ZnS films increases linearly with concentration of thiourea increase in the range of 0,025…0,10 M. Further increasing of thiourea concentration in the working solution to 0,25 M does not leads to increase the weight of zinc, and leads to excess of consumption of reagents. Thus, the optimum value of the concentration of thiourea is selected 0,10 M.

The mass of zinc in the ZnS films increases linearly with the temperature of the synthesis increase from 50 to 80 °C. The growth stops at a temperature above 80 °C due to the rapid exhaustion of the working solution at these temperatures having other deposition parameters constant. Analysis of the morphology of the film surface (Fig. 4) showed that there is a small number of defects on the surface of ZnS films at lower deposition temperatures (50…70 °C). The number of defects is much higher at higher temperatures (80…90 °C). Thus, the optimal temperature is 70 °C.

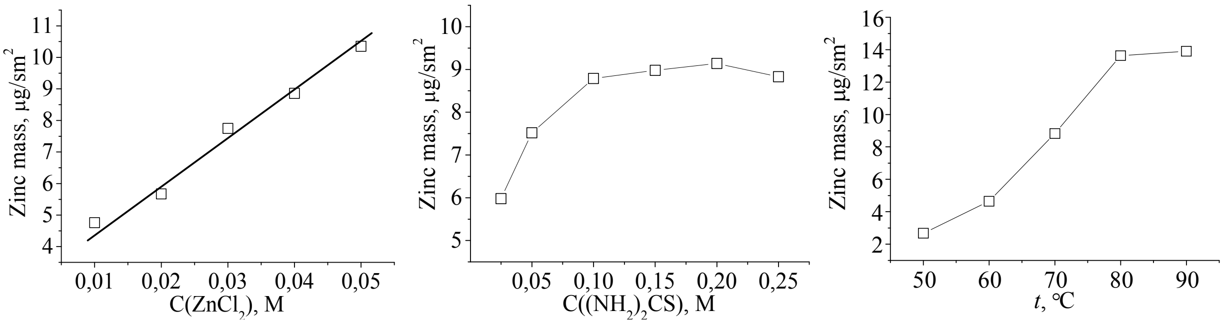

Fig. 2. The change dependence of zinc weight per unit area in ZnS films on the initial concentration of zinc-containing salt, the concentration of thiourea and deposition temperature

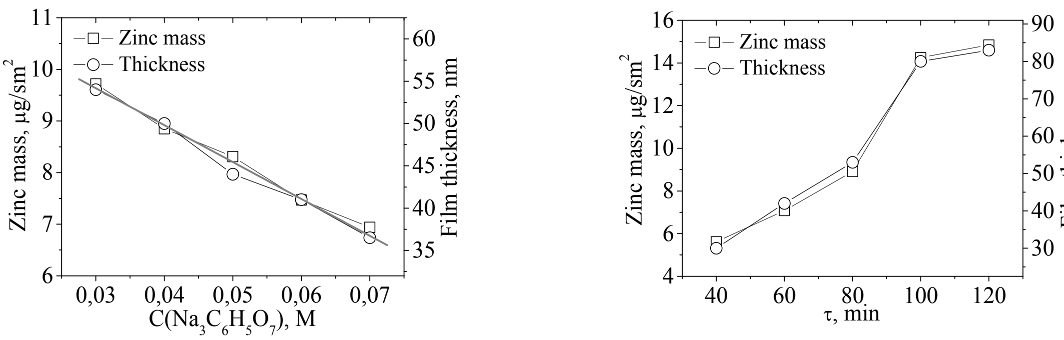

Fig. 3 The change dependence of zinc weight per unit area and the thickness in ZnS films on the concentration of sodium citrate and duration of the precipitation

The change of mass of zinc in the ZnS films is linear in case of varying concentration of complexing agent trisodium citrate. When concentration of $Na_3C_6H_5O_7$ in the working solution is less than 0,04 M there was registered the formation of zinc hydroxide. When the concentration of $Na_3C_6H_5O_7$ is above 0,04 M the mass of zinc in the ZnS films decreases linearly. Thus, the optimum value of the trisodium citrate concentration for this series is 0,04 M.

The mass of zinc in ZnS films increases almost linearly with increase of deposition time in the time interval of 40…100 minutes. In case of 120 minutes time interval there is a slight increase of zinc weight as a result of the depletion of the working solution. Analysis of the surfaces films morphology (Fig. 4) showed that there is a small number of defects observed on the surface of ZnS films for deposition duration of 80 minutes. And the number of defects increases dramatically for 100…120 minutes of deposition. Such an increase corresponds to a weight jump of zinc at the range of 80…100 min. With a maximum duration (120 min) among defects there was seem the visible cracks of ZnS film surface. Thus, the optimum value of the deposition time is 80 min.

The thickness of ZnS films was determined depending on the amount of complexing agent of trisodium citrate and deposition time. There is the same character results when comparing the results obtained thickness and weight of zinc (Fig. 3). This allows to evaluate and predict the thickness of ZnS films by known weight value of zinc in them. That is a good alternative if you can't, for whatever reasons, to make a direct measurement of ZnS films thickness. The study of element composition of zinc sulfide films has shown that the atomic ratio of zinc to sulphur in the films is close to stoichiometric, with a slight excess of zinc atoms that can be explained by the presence of surface defects. It is found that the registered formations on the surface are the agglomerates of zinc sulfide with an excess of zinc atoms which are formed in the volume of work solution and are adsorbed on the surface of the film at the final stages of deposition.

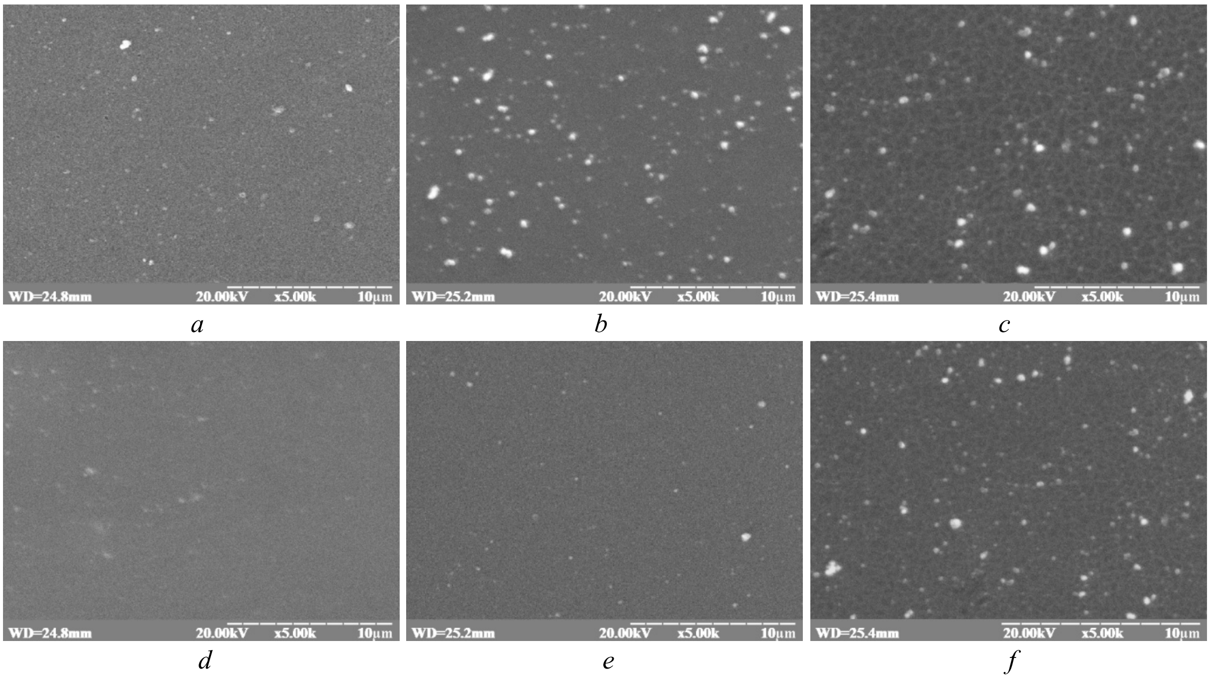

Fig. 4. The surface morphology of ZnS films obtained using trisodium citrate with different deposition duration (a — 80 minutes, b — 100 minutes, c — 120 minutes) and with different deposition temperatures (d — 50 °C, e — 70 °C, f — 90 °C)

From the mentioned studies it can be argued that the optimum conditions for deposition of ZnS films is the molar ratio of zinc salt, trisodium citrate and thiourea in the working solution of 0,04 : 0,04 : 0,10 M respectively. A deposition time is 80 min with a temperature 70 °C.

The three-dimensional AFM image of the film ZnS (Fig. 5) synthesized in the mentioned optimal conditions shows that the film is homogeneous, smooth and solid, with a small amount of surface defects. The presented histogram of the height of crystal grains above the surface of the substrate indicates that the film contains a large number of densely packed particles of the same size and, hence, has a small amount of voids. It can be concluded that the optimal conditions for ZnS films deposition are selected definitely good.

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

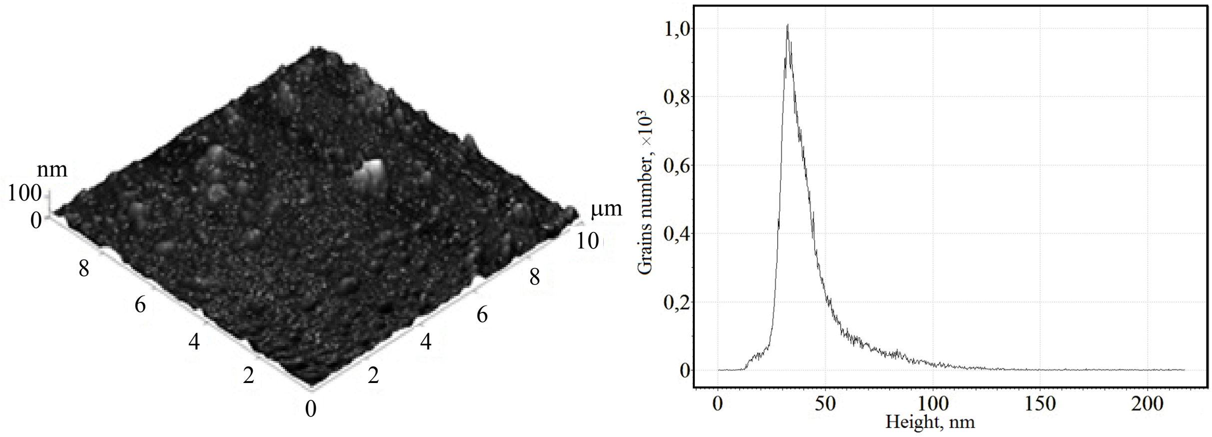

Fig. 5. The three-dimensional AFM image of the surface and the distribution histogram of the crystal grains height above the surface of the ZnS films using optimum conditions

The optical spectra of light transparency $T(\lambda)$ of ZnS films for wavelengths from 200 to 700 nm had been studied. It was found that there is a rapid increase in light transmission from 0 to 70 % for wavelengths greater than 300 nm. It was established the presence of the fundamental absorption edge localized in the area of 3,65 eV for ZnS films from the dependence of the absorption of ZnS films in the coordinates $(\alpha \cdot h\nu)^2$, $h\nu$ and this corresponds to the literature data for zinc sulfide [4].

Conclusions. The ZnS films were synthesized in this work using chemical deposition method from aqueous caustic of zinc-containing salt and using trisodium citrate as a complexing agent. The phase composition, surface morphology, optical properties and thickness of synthesized ZnS films were studied. The research demonstrated the possibility of using the method of stripping voltammetry to control the process of chemical deposition of ZnS thin films from aqueous caustics. The dependences of zinc mass in the ZnS films on deposition conditions were defined. The same nature change of ZnS films thickness and weight of zinc in ZnS films was showed. That makes possible to predict and get the platting of specified thickness. The optimal parameters for ZnS films synthesis were determined on the basis of research results. That are the molar ratios of the starting reagents in the working solution: zinc salt, trisodium citrate, thiourea — 0,04 : 0,04 : 0,10 moles respectively with a deposition time of 80 min and a temperature 70 °C. The ensuring of specified synthesis conditions allows getting thin, smooth, solid ZnS films suitable for use as semiconductor films.

Література

1. Контроль процесу осадження тонких плівок CdS з водного розчину кадмій ацетату методом інверсійної вольтамперометрії / П.Й. Шаповал, Р.Р. Гумінілович, Й.Й. Ятчишин [та ін.] // Вісник Національного університету «Львівська політехніка». Хімія, технологія речовин та їх застосування. — 2012. — № 726. — С. 45 — 48.
2. Оптимальні умови синтезу тонких плівок CdSe з водного розчину кадмій хлориду методом хімічного поверхневого осадження / Р.Р. Гумінілович, П.Й. Шаповал, Й.Й. Ятчишин [та ін.] // Вісник Національного університету «Львівська політехніка». Хімія, технологія речовин та їх застосування. — 2012. — № 726. — С. 52 — 55.
3. PowderCell 2.3 — powder pattern calculation from single crystal data and refinement of experimental curves [Електронний ресурс] / W. Kraus, G. Nolze // Federal Institute for Materials Research and Testing. — Режим доступу: http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/e_cell.html (Дата звернення: 14.05.2015).
4. Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films / S.M. Pawar, B.S. Pawar, J.H. Kim, *etc.* // Current Applied Physics. — 2011. — Vol. 11, Issue 2. — PP. 117 — 161.

References

1. Shapoval, P.I., Guminilovich, R.R., Yatchyshyn, I.I., Kus'nezh, V.V., & Il'chuk, G.A. (2012). Controlling the deposition process of CdS thin films from aqueous solutions of cadmium acetate by method of stripping voltamperometry. *Herald of National University "Lvivska Politechnika": Chemistry, Technology of Materials and their Applications*, 726, 45–48.
2. Guminilovich, R.R., Shapoval, P.I., Yatchyshyn, I.I., Kus'nezh, V.V., & Il'chuk, G.A. (2012). Optimal conditions for synthesis of CdSe thin films from aqueous solutions of cadmium chloride by method of chemical surface deposition. *Herald of National University "Lvivska Politechnika": Chemistry, Technology of Materials and their Applications*, 726, 52–55.
3. Kraus, W., & Nolze, G. (2000). PowderCell 2.3 — powder pattern calculation from single crystal data and refinement of experimental curves. *Federal Institute for Materials Research and Testing*. Retrieved from http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/e_cell.html
4. Pawar, S.M., Pawar, B.S., Kim, J.H., Joo, Oh-Shim, & Lokhande, C.D. (2011). Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films. *Current Applied Physics*, 11(2), 117–161.

Received June 19, 2015
Accepted September 28, 2015