CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 10, No. 3, 2016 Chemical Technology

Pavlo Shapova [1], Martyn Sozanskyi[1], Iosyp Yatchyshyn[1], Bogdan Kulyk[2],
Mykhaylo Shpotyuk[3] and Roman Gladyshevskii[4]

THE EFFECT OF DIFFERENT COMPLEXING AGENTS ON THE PROPERTIES OF ZINC SULFIDE THIN FILMS DEPOSITED FROM AQUEOUS SOLUTIONS

[1] Department of Analytical Chemistry, Lviv Polytechnic National University,
12 S. Bandera St., 79013 Lviv, Ukraine; pavlo.y.shapoval@lpnu.ua
[2] Scientific-Technical and Educational Center of Low Temperature Studies,
Ivan Franko National University of Lviv, 50 Dragomanova St., 79005 Lviv, Ukraine
[3] Department of Semiconductor Electronics,
Lviv Polytechnic National University, 12 S. Bandera St., 79013 Lviv, Ukraine
[4] Department of Inorganic Chemistry, Ivan Franko National University of Lviv,
6 Kyryla i Mefodiya St., 79005 Lviv, Ukraine

Received: December 12, 2015 / Revised: February 02, 2016 / Accepted: May 12, 2016

© Shapoval P., Sozanskyi M., Yatchyshyn I., Kulyk B., Shpotyuk M., Gladyshevskii R., 2016

Abstract. The zinc sulfide (ZnS) thin films were prepared on glass substrates by chemical bath deposition using the aqueous solutions of zinc chloride, thiourea, pH regulator and complexing agent (ammonia and hydrazine hydrate, trisodium citrate or sodium hydroxide). The calculations of boundary conditions for formation of zinc sulfide and zinc hydroxide were made at various zinc salt concentrations with different complexing agents. The structural, morphology and optical properties of the ZnS thin films were investigated. The thickness of ZnS films was measured and the recalculation of zinc mass per cm^2 of the substrate surface was held for comparison. The deposition mechanism is discussed.

Keywords: zinc sulphide, thin films, chemical bath deposition, optical properties, morphology analysis, growth mechanism.

1. Introduction

Zinc sulfide (ZnS) films are an alternative material for the manufacture of wide-bandgap "windows" of thin film photosensitive elements (TFPE). ZnS is not toxic and is capable of transmitting light with wavelengths below 520 nm, in contrast to the cadmium sulfide (CdS), which is considered as the most effective material for the manufacture of TFPE wide-bandgap "windows". Thin-film ZnS-based solar cells have the efficiency of photoconversion ~14.4–15.7 % [1-2].

Chemical bath deposition (CBD) is technologically convenient method of zinc sulfide films synthesis. Synthesis of metal sulfides at the hydrochemical deposition is based on interaction reactions of the metal salt, complexing agent and thiourea in an aqueous solution. The sulfides formation is the summation of chemical reactions, mechanism of which has not been studied yet. That is why, even today, prescription-experimental approaches dominate in the hydrochemical synthesis. The general information, which is given in most publications, does not describe the chemism of the process, and, as a rule, find regularities in a separately-taken case of synthesis. For example, ZnS films, which are obtained under different conditions using the same complexing agents, have different bandgap values (E_g), which vary from 3.5 to 3.98 eV [3-5].

The aim of our work was to conduct the complex research, which should include: preliminary calculation of formation conditions of zinc sulfide films using the reference thermodynamic data; application of modern theoretical methods of calculation and modeling of possible flow ways of chemical reactions; experimental methods for studying the composition, structure and morphology of the synthesized semiconductor thin films. Analysis of obtained theoretical and experimental results will allow to colligate the conditions of ZnS deposition with properties of the obtained semiconductor films. It is the actual task of thin film technology, solution of which allows to control the CBD process of zinc sulfide thin films.

2. Experimental

2.1. Materials

Freshly prepared 1 M solution of zinc chloride ($ZnCl_2$) and 1 M solution of thiourea ($(NH_2)_2CS$) were used for the synthesis of ZnS films. The following solutions were used as complexing agents: 0.5 M trisodium citrate solution ($Na_3C_6H_5O_7$); 25 % solution of ammonia ($NH_3 \cdot H_2O$) and/or 80 % solution of hydrazine hydrate ($N_2H_4 \cdot H_2O$); saturated solution of sodium hydroxide (NaOH). The $NH_3 \cdot H_2O$ and NaOH were used as regulators of pH.

ZnS film deposition was carried out on pre-cleaned glass substrates with a size of 18x18 mm. For this, working solution was prepared under stirring by sequentially adding of freshly prepared solutions of zinc salt, complexing agent, pH adjuster, thiourea and distilled water. Deposition was carried out in a glass bath for 40–120 min at 343–353 K. Thereafter, the substrates were taken out from the bath, washed with distilled water and dried in the air.

Chemical composition of working solutions was different by depending of various complexing agents. The order of recording here and further corresponds to the order of mixing of the reactants.

Working solution No.1: 0.2–1.0 ml of 1 M solution of $ZnCl_2$; 1.2–2.4 ml of 0.5 M solution $Na_3C_6H_5O_7$; 0.2 ml of 14.28 M solution of $NH_3 \cdot H_2O$; 14.4–16.4 ml of distilled water and 2.0 ml of 1 M solution $(NH_2)_2CS$. The total volume of solution was 20.0 ml; pH = 9.6.

Working solution No.2: 2 ml of 1 M solution of $ZnCl_2$; 0.2–2.0 ml of 14.28 M solution of $NH_3 \cdot H_2O$ and 80 ml of 80 % $N_2H_4 \cdot H_2O$; 2.0–7.6 ml of distilled water and 10 ml of 1 M solution ($(NH_2)_2CS$). The total volume of solution was 20.0 ml; pH = 10.1–11.0.

Working solution No.3: 0.2–1.0 ml of 1 M solution of $ZnCl_2$; 0.5–3.0 ml of NaOH saturated solution; 15.0–18.3 ml of distilled water and 1 ml of 1 M solution ($(NH_2)_2CS$). The total volume of solution was 20.0 ml; pH = 11.4–12.2.

2.2. Analysis

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

Optical transmission spectra of zinc sulfide films were recorded on a Lambda 25 spectrophotometer (Perkin-Elmer) in the 200–700 nm wavelength range. The maximum associated error in the optical transmission detection does not exceed ±0.3 %.

Investigation of surface morphology of the films was performed using REMMA-102-02 raster scanning electron microscope (SEM) in modes of reflected and secondary electrons and Solver P47 PRO (NT-MDT) atomic-force scanning probe microscope (AFM). AFM studies were carried out by semi-contact and contact methods with the scanning frequency of 1 Hz by using a silicon probe, type NSG 10 A, with a radius of curvature of the tip 10 nm. All studies were performed in the air. The processing of experimental data and calculation of the surface morphology parameters were performed using Image Analysis 2 software package (NT-MDT).

Determination of zinc contents in obtained films was performed by the method of stripping voltammetry (analyzer AKV-07 MK, Akvilon). The experimental procedure is described more precisely in [7].

The film thickness was measured using DEKTAK IIA (SLOAN) profilometer.

The semiempirical method RM7 was used for the calculations of possible mechanisms of the formation of ZnS films. All quantum-chemical calculations were carried out within MOPAC 2012 [8] and graphical interface Winmostar [9] PC programs.

3. Results and Discussion

Zinc forms complex compounds with many substances. Using of ligands with different force and changing their concentrations allow to adjust the concentration of uncomplexed zinc ions ($a_{Zn^{2+}}$), which was calculated, in working solution, by the equation:

$$a_{Zn^{2+}} = \frac{1}{1 + \frac{[L]}{k_1} + \frac{[L]^2}{k_{1,2}} + \ldots + \frac{[L]^n}{k_{1,2,\ldots n}}}$$

where $[L]$ – free ligand concentration, $k_{1,2,\ldots n}$ – instability constants of comprehensive forms of the metal. $\lg K([Zn(NH_3)_4]^{2+}) = 9.08$; $\lg K([Zn(H_2NNH_2)_4]^{2+}) = 3.78$; $\lg K([Zn(OH)_4]^{2-}) = 14.8$ and $\lg K([Zn(C_6H_5O_7)]^{-}) = 4.98$ values of stability constants were used for calculations.

The minimum concentration of zinc salt, which is necessary for formation the zinc sulfide, was calculated by the following equation [10]:

$$pC^0_{Zn} = pSP_{ZnS} - pa_{Zn^{2+}} -$$

$$-\left(pK_{H_2S} - 2pH + \frac{1}{2} pK_{Th} + \frac{1}{2} p[Th]_H + \frac{1}{2} p\frac{b_{CAm}}{b_{Th}} \right)$$

where p – indicator (negative decimal logarithm); C^0_{Zn} – minimum concentration of zinc salt, which is necessary for formation a solid phase; SP_{ZnS} – solubility product of

ZnS; K_{H2S}, K_{Th} – dissociation constants of hydrogen sulfide and thiourea derivatives, respectively; β_{CAm} and β_{Th} – instability constants of cyanamide and thiourea complexes, respectively.

The boundary conditions for formation of zinc sulfide (ZnS) and zinc hydroxide ($Zn(OH)_2$) (Fig. 1) are shown for different complexing agents.

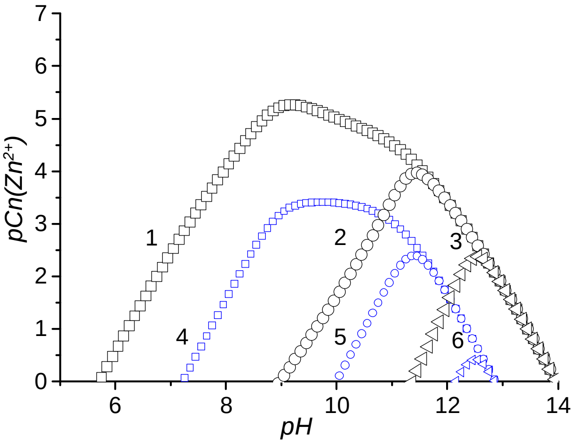


Fig. 1. Boundary conditions of ZnS and $Zn(OH)_2$ formation in the system $Zn^{2+} – L_x – (NH_2)CS$, where L_x – trisodium citrate (regions limited by *curves* 1 and 4, respectively); L_x – ammonia/hydrazine hydrate (regions limited by *curves* 2 and 5, respectively); L_x – sodium hydroxide (regions limited by *curves* 3 and 6, respectively)

Maximum values of $pC_n(Zn^{2+})$, that respond to minimum values of zinc salt concentration in the initial working solution, are observed at such pH values, when protonation and formation of hydroxocomplexes are minimal. This region is the largest for trisodium citrate and keeps the maximum values in the pH range = 9.5–12. The plateau region is absent on depending curve for a pair of ammonia/hydrazine and sodium hydroxide, and the maximum values of $pC_n(Zn^{2+})$ is achieved at pH of ~ 11 and pH ~ 13, respectively. This imposes restrictions on the possible pH changes at the process of synthesis and results in non-target products forming.

The protonation will grow at decreasing of the solution pH. The hydrolysis of thiourea and the possibility of sulfides formation will decrease. The concentration of hydroxyl ions will grow together with the increasing hydrolysis of thiourea under the increase the solution pH above the maximum; this led to the formation of hydroxozincates, which can be decomposed then to form zinc hydroxide or zinc oxide. This effect will be more pronounced with a sharp increase of temperature, which will take place under the heating of small amounts of working solutions. It was observed by us earlier at trying to use the method of chemical surface deposition for synthesis of zinc sulfide [11]. The phases of hexagonal modifications of zinc sulfide ZnS (wurtzite), impurities of cubic modification of ZnO (sphalerite) and zinc hydroxide $Zn(OH)_2$ were present in the films synthesized using trisodium citrate. The phases of zinc oxosulfide ZnS_xO_{1-x} (wurtzite) and impurities of phase ZnO (sphalerite) were presented in the films deposited using $NH_3{\cdot}H_2O$.

ZnS deposition may begin with initial concentration of zinc salt more than $1{\cdot}10^{-6}$ M at using trisodium citrate as a complexing agent, more than $1{\cdot}10^{-4}$ M at using hydrazine/ammonia couple and $1{\cdot}10^{-3}$ M sodium hydroxide, according to Fig. 1. Deposition of zinc hydroxide may begin at the two orders greater concentration of initial zinc salt in respect to above described conditions.

In fact, we failed to get the films at the calculated concentrations. The minimum concentration of initial zinc salt was $1{\cdot}10^{-2}$ M for deposition of solid homogeneous ZnS thin films. The decrease of concentration led to a significant increase of the deposition time, being inappropriate.

The surfaces of substrates were completely covered by the films after the deposition process. The deposited films were homogeneous and had characteristic mirror lustre, when using trisodium citrate or sodium hydroxide as complexing agents.

In the case of deposition using a solution of ammonia or an ammonia/hydrazine pair, the highest rate of solid phase formation was observed in the bulk solution, the deposited films were white and had no mirror lustre. It is an evidence of formation of the coatings, contaminated by a significant amount of zinc hydroxide or zinc oxide under given conditions.

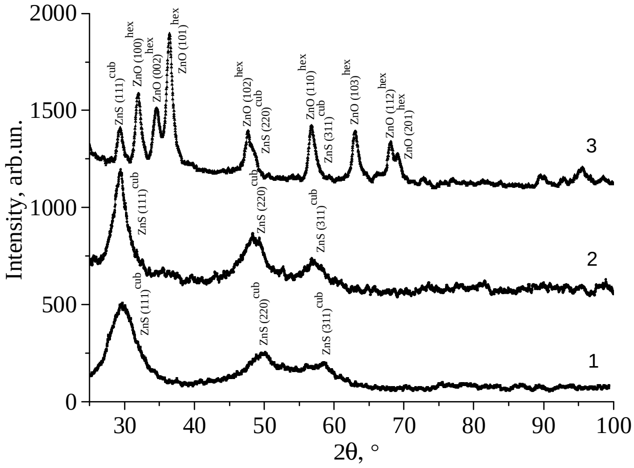


Fig. 2. Experimental profiles of diffractograms of ZnS films obtained using various complexing agents: trisodium citrate (1); sodium hydroxide (2) and hydrazine hydrate/ammonia (3)

The phase composition was set by X-ray-phase analysis of the synthesized samples (Fig. 2).

Phase of ZnS compound was defined in a cubic modification without any significant visible impurities of other phases in the films with $Na_3C_6H_5O_7$ and NaOH as complexing agents. ZnS phase (sphalerite) and a significant amount of ZnO hexagonal modification are included to the films, obtained with using $N_2H_4{\cdot}H_2O/NH_3{\cdot}H_2O$. Crystallographic characteristics of the obtained compounds are given in Table 1.

The transmission spectra of thin films, synthesized using various complexing agents, show the rapid increase in optical transmission for ZnS at wavelengths greater than 300 nm, but characters of its change are different (see Fig. 3). There is a sharp rise to the saturation of optical transmission for the films, deposited in the presence of $N_2H_4{\cdot}H_2O/NH_3{\cdot}H_2O$, while for the films, deposited in the presence of $Na_3C_6H_5O_7$ and NaOH, the transmission grows smoothly during the transition from the short-wave to long-wave region.

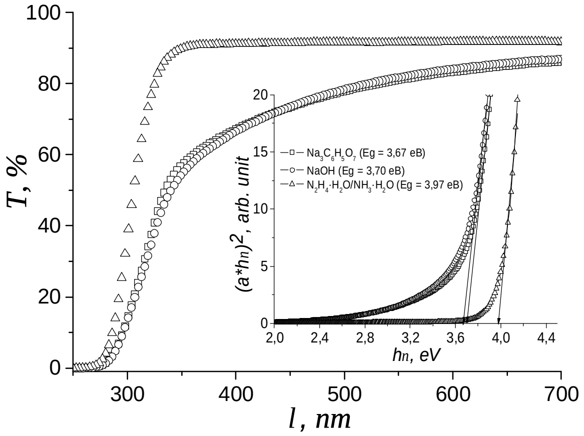


Fig. 3. Spectral dependences of optical transmission (*T*, %) of ZnS films synthesized using various complexing agents on glass substrates. Dependence $(\alpha{\cdot}h\nu)^2 = f(h\nu)$ is on the inset, where α – optical absorption coefficient

Absorption spectra of ZnS films show the presence of fundamental optical absorption edge, localized near 3.7 eV for ZnS films obtained with using trisodium citrate and sodium hydroxide, in the coordinates $(a{\cdot}hn)^2$ – *hn* (inset in Fig. 3). The shift of fundamental optical absorption edge toward the high-energy range was observed for the films synthesized using ammonium hydroxide and hydrazine hydrate, as well as optical bandgap value increases to 3.97 eV. Such spectral dependence can be explained by the presence of significant amount of zinc oxide in the films (which was detected by X-ray analysis) and different structure of films packaging, which was determined by the surface morphology investigations.

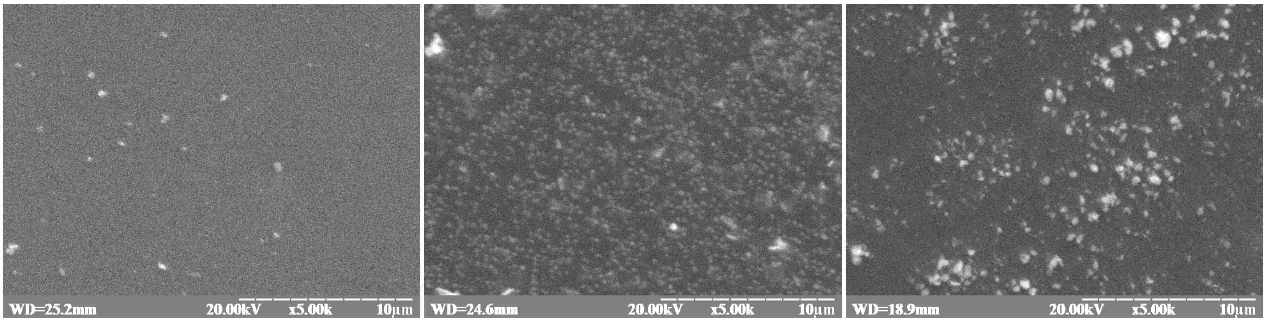
Spectroscopic studies of surface morphology of the films show that films deposited with using various complexing agents, are completely covering the substrate, they are homogeneous and solid over the entire area (Fig. 4). The heavy phase particles are observed on the films surface, synthesized with trisodium citrate and sodium hydroxide, while in the films obtained in the presence of ammonium hydroxide and hydrazine hydrate, inclusion of ZnO are contained throughout the full volume, which indicates its formation during the reaction.

Analysis of surface morphology, obtained in the AFM, and the calculated histograms of the crystal grains height over the total surface of the films (Fig. 5) allow to affirm that deposition method and nature of complexing agent influence the ZnS films structure. Films deposited with using $Na_3C_6H_5O_7$ have the minimum roughness, because they are packed by the crystal grains of smallest sizes (5–30 nm), a major amount of which has the size of ~22 nm, *i.e.* have the densest packing. The grain heights are the biggest over the total surface of the films, deposited in NaOH environment, and the grains themselves have a nearly spherical form. In addition, the grains of irregular forms, the size of which is 100 nm and more, were found on films surface. As it has appeared, these formations are crystals of NaCl. Films were soaked in warm distilled water for 60 min to get rid of NaCl crystals and as a result the absolutely clean surfaces without impurities were obtained. Films deposited using $N_2H_4{\cdot}H_2O/NH_3{\cdot}H_2O$ are packed by ZnS and ZnO crystallites which height above the surface is in the range of 10–60 nm.

Table 1

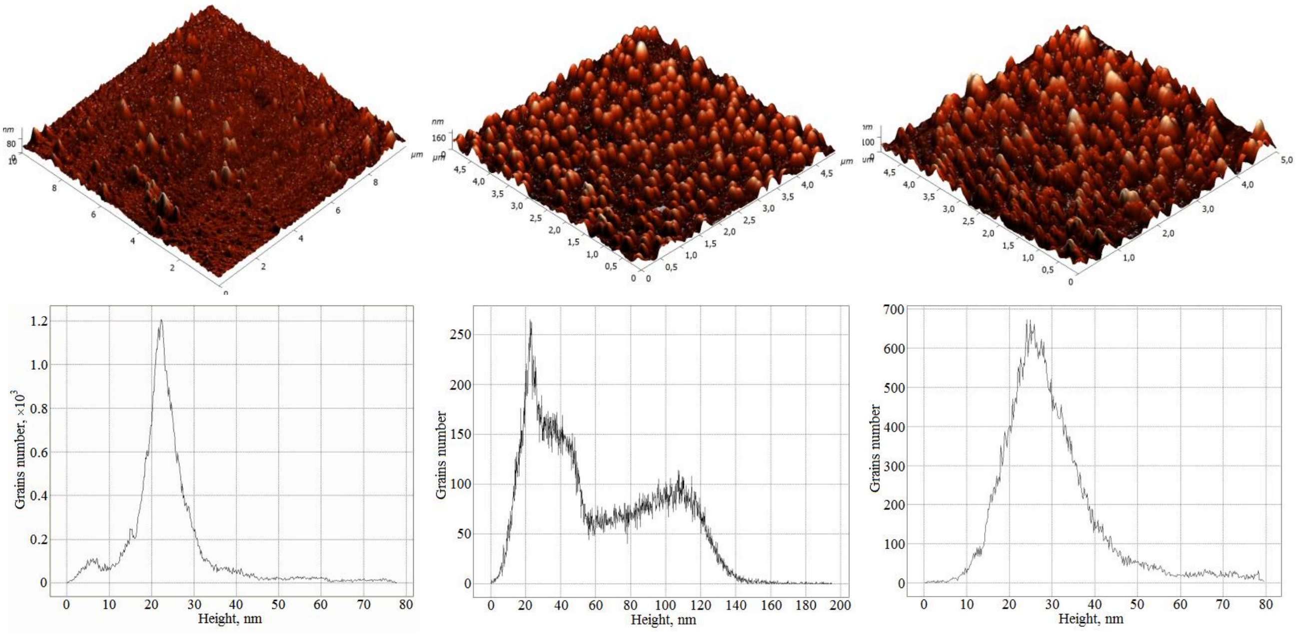
Crystallographic characteristics of compounds in the films obtained using various complexing agents

$Na_3C_6H_5O_7$	NaOH	$N_2H_4{\cdot}H_2O/NH_3{\cdot}H_2O$
(1) ZnS (cub) Structural type – ZnS; Space group – *F*-43*m* Pearson symbol – *cF*8 *a* = 0.5323(2) nm	***(1) ZnS (cub)*** Structural type – ZnS Space group – *F*-43*m* Pearson symbol – *cF*8 *a* = 0.5373(2) nm	***(1) ZnO (hex)*** Structural type – ZnO Space group – $P6_3mc$ Pearson symbol – *hP*4 *a* = 0,32473(3) nm; *c* = 0.52026(6) nm) ***(2) ZnS (cub)*** Structural type – ZnS Space group – *F*-43*m* Pearson symbol – *cF*8; *a* = 0.5351(2) nm



1 2 3

Fig. 4. SEM surface morphology of ZnS films and calculated histogram of the crystal grains height deposited with using various complexing agents: $Na_3C_6H_5O_7$ (1); NaOH (2) and $N_2H_4{\cdot}H_2O/NH_3{\cdot}H_2O$ (3)



1 2 3

Fig. 5. AFM surface morphology of ZnS films and calculated histogram of the crystal grains height deposited with using various complexing agents: $Na_3C_6H_5O_7$ (1); NaOH (2) and $N_2H_4{\cdot}H_2O/NH_3{\cdot}H_2O$ (3)

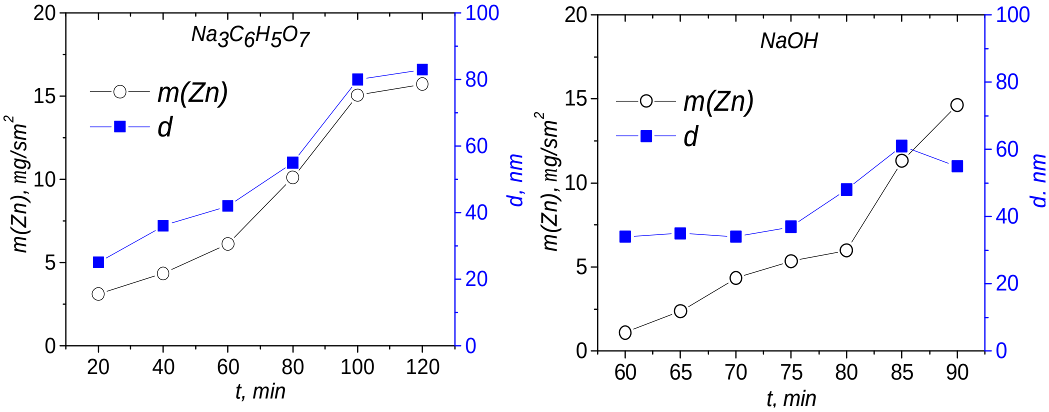


Fig. 6. Dependence of zinc mass change in the ZnS films and their thickness on deposition time ($C(Na_3C_6H_5O_7) = 0.04$ M and $C(NaOH) = 0.8$ M)

Microanalysis of ZnS films show that using of trisodium citrate, as a complexing agent with the ratio of $C(Na_3C_6H_5O_7):C(ZnCl_2) = 1:1$ leads to the atomic ratio of Zn:S ~ 1. The increase or decrease in complexing agent concentration leads to the increase in numerical value of Zn/S.

The atomic ratio of Zn:S ~ 1 is achieved only at 120-fold excess of NaOH and it remains up to 200-fold excess in the case of using sodium hydroxide. Excess sulfur atoms are observed in all synthesized films, unlike the previous case. Results of microanalysis of ZnS films synthesized from solutions containing $N_2H_4{\cdot}H_2O/NH_3{\cdot}H_2O$ as complexing agents regularly showed the prevailing content of zinc atoms.

The differences are also observed in studies of changing the zinc mass in the ZnS films and their thickness in respect to deposition time (Fig. 5). An actual thickness of synthesized films (*d*, nm) was measured and the recalculation of zinc mass *m*(*Zn*) on cm^2 on the surface of substrate, was held on the voltammetric determination results of zinc content for comparison, provided that films are uniform and they are completely covered surface substrate.

Deposition with trisodium citrate was started quickly and continued longer (120 min) than with sodium hydroxide (90 min). The maximum thickness of deposited films per one cycle was 80 nm, as well as in the case of NaOH – 60 nm (Fig. 6). An inconsistency between actual measured thickness and zinc content in the case of NaOH, as a complexing agent, is observed up to achieving the film thickness of ~ 35 nm. By using trisodium citrate, the zinc mass growth and film thickness are suspended synchronously that is explained by the depletion of the working solution at the final stages of deposition. The formed films are characterized by a small number of particles, adsorbed on their surface. In the case of using sodium hydroxide, the surface of the films is covered by ZnS particles from the volume which makes impossible their further increasing after achievement the maximum thickness in the vicinity of 60 nm.

The differences of structural and optical properties of the films confirm the influence of complexing agent nature on the deposition process. The difference of compositional and morphological parameters indicates various possible mechanisms of the formation of ZnS films. Therefore, quantum-chemical modeling of possible ways of chemical reactions in aqueous solution was held. The calculation was done according to the order of mixing reagents.

The formation of corresponding soluble complexes: $[Zn(NH_3)_4]^{2+}$, $[Zn(H_2NNH_2)_4]^{2+}$, $[Zn(OH)_4]^{2-}$, $[Zn(C_6H_5O_7)]^{-}$ occurs after adding the complexing agent to the zinc salt ($ZnCl_2$) solution. A minor amount of ammonium hydroxide is added to the solution to provide pH = 9.6 in the case of using trisodium citrate. Formed complexes behave differently after adding thiourea to the solution.

In the case of using $N_2H_4{\cdot}H_2O/NH_3{\cdot}H_2O$ or NaOH, they have two functions in the reaction bath: ligand which forms a complex with zinc and regulator of pH for thiourea hydrolyzes. Formed complexes are destroyed with forming zinc hydroxide, in which zinc atom is coordinated with sulfur atom of thiourea to form a reactive complex. Its thermal destruction leads to the formation of final products through a number of transition states:

$$\left[Zn(NH_3)_4\right]^{2+} + SC(NH_2)_2 + 2OH^- \longrightarrow$$

$$\longrightarrow \left[(OH)_2 Zn \cdots\cdots SC(NH_2)_2\right] + 4NH_3 \uparrow$$

$$\left[Zn(N_2H_4)_3\right]^{2+} + SC(NH_2)_2 + 2OH^- \longrightarrow$$

$$\longrightarrow \left[(OH)_2 Zn \cdots\cdots SC(NH_2)_2\right] + 3N_2H_4 \uparrow$$

$$\left[Zn(OH)_4\right]^{2-} + SC(NH_2)_2 \longrightarrow$$

$$\longrightarrow \left[(OH)_2 Zn \cdots\cdots SC(NH_2)_2\right] + 2OH^-$$

$$\left[(OH)_2 Zn \cdots\cdots SC(NH_2)_2\right] \xrightarrow{t,\,^\circ C} ZnS + HNCNH + 2H_2O$$

Decreasing the ammonium hydroxide or hydrazine hydrate concentration creates favorable conditions for the formation of zinc oxide during the reaction in consequence of pH instability particularly at the final stages of deposition. The pure ZnS is formed in the case of using sodium hydroxide but the surface of synthesized films is crumbly. Furthermore, the viscosity of working solution increases with increasing of NaOH concentration accompanied by the increase in ZnS particle size.

In the case of using trisodium citrate – it plays only the ligand role. The reactive-able intermediate dihydroxy-zincate complex is formed in an alkaline medium. After addition of thiourea it is coordinated through a zinc atom with sulfur atom. Then, the formed structure, by going through two intermediate states, is destroyed with forming zinc sulfide, citrate ions, two water molecules, and diimide, which trasforms into the cyanamide form due to tautomerization in the solution. Schematically, this process can be written as:

$$Zn^{2+} + Cytr^{3-} + 2OH^- \longrightarrow [Zn(OH)_2Cytr]^{3-}$$

$$[Zn(OH)_2Cytr]^{3-} + SC(NH_2)_2 \longrightarrow$$

$$\longrightarrow [(NH_2)_2CS \cdots\cdots Zn(OH)_2Cytr]^{3-}$$

$$[(NH_2)_2CS \cdots\cdots Zn(OH)_2Cytr]^{3-} \xrightarrow{t,\,^\circ C}$$

$$\xrightarrow{t,\,^\circ C} ZnS + Cytr^{3-} + NHCNH + 2H_2O$$

It can be confirmed that the nature of complexing agent determines the mechanism passage of synthesis reaction of zinc sulfide films based on experimental data and held calculations. Formation and growth of film begins with the formation of nuclei on the surface of substrate due to reaction of zinc hydroxide or zinc dihydroxy-citrate with thiourea. The orientation of thiourea complexes occurs on the active centers of its surface at the interaction with substrate. Complex particles are capable to interact with the active centers of substrate, that provides the binding of sulfide with substrate. The nature of this interaction determines the nature of film adhesion.

4. Conclusions

In this work an attempt to consider the problems of synthesis of zinc sulfide thin films as a whole was done with the aim of manufacturing the common rules and approaches of the control of their hydrochemical synthesis process. Effect of nature and complexing agent concentration on the ZnS films properties was proved. In practice trisodium citrate should be most expedient for use for the synthesis of ZnS thin solid films. That is why the films, synthesized under optimized conditions, have properties that completely meet the requirements for the manufacturing of TPFE wide-band “windows”. The use of ammonium hydroxide or hydrazine hydrate is inexpedient, due to their insalubrity, inability to ensure stable conditions of synthesis and greater probability of formation byproduct – ZnO. Synthesis with using sodium hydroxide provides its significant cost, the obtaining films are composed of ZnS cubic modification without any significant visible impurities of other phases but they have a significantly lower adhesion because of other growth mechanism of the coating.

References

[1] Ennaouia A., Eiselea W., Lux-Steinera M. *et al.*: Thin Solid Films, 2003, **431-432**, 335.

[2] Gangopadhyay U., Kim K., Dhungel S. *et al.*: Adv. OptoElectron., 2007, **2008**, 1.

[3] Shin S., Kang S., Yun J. *et al.*: Sol. Energ. Mat. Sol. C., 2011, **95**, 856.

[4] Kang S., Shin S., Choi D. *et al.*: Curr. Appl. Phys., 2010, **10**, 473.

[5] Louh R. and Wu W.: Adv. Mat. Res., 2008, **51**, 125.

[6] Kraus W. and Nolze G.: PowderCell for Windows (version 2.4). Federal Institute for Materials Research and Testing, Berlin 2000.

[7] Shapoval P., Guminilovych R. and Yatchyshyn I.: Chem. Chem. Technol., 2013, **7**, 345.

[8] Stewart J.: Program Package MOPAC2009 (http://www.openmopac.net).

[9] Senda N.: Program Package Winmostar (http://winmostar.com).

[10] Tulenin S., Bakhteev S., Yusupov R. *et al.*: Zh. Fiz. Khim., 2013, **87**, 1791.

[11] Shapoval P., Sozanskyi M., Yatchyshyn I., *et al.*: Visnyk Lviv. Polytech. Nats. Univ., 2014, **787**, 31.

ВПЛИВ ПРИРОДИ КОМПЛЕКСОУТВОРЮВАЧА НА СТРУКТУРУ І ВЛАСТИВОСТІ ТОНКИХ ПЛІВОК ЦИНК СУЛЬФІДУ, ОСАДЖЕНИХ З ВОДНИХ РОЗЧИНІВ

Анотація. *Методом хімічного осадження ванн отримано тонкі плівки цинк сульфіду ZnS на скляних підкладках з використанням водних розчинів цинк хлориду, тіосечовини, регулятора pH і комплексоутворювача (аміаку і гідрату гідразину, тринатрій цитрату або натрій гідроксиду). Розраховано граничні умови для утворення цинк сульфіду і цинк гідроксиду за різних концентрацій солі цинку з різними комплексоутворювачами. Досліджено структурні, морфологічні та оптичні властивості тонких плівок ZnS. Виміряно товщину плівок ZnS і для порівняння проведено перерахунок маси цинку на см^2 поверхні підкладки. Обговорений механізм осадження.*

Ключові слова: *цинк сульфід, тонкі плівки, хімічне осадження з ванн, оптичні властивості, аналіз морфології, механізм росту.*