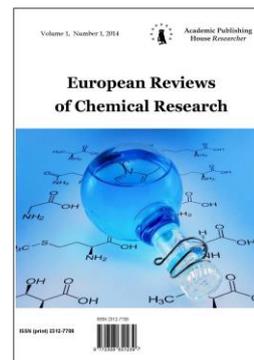


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Ligand Background of the Reaction Mixture as a Factor of the CdS – PbS thin Films Formation by Chemical Bath Deposition

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Abstract

The concentration planes of lead and cadmium sulphide formation in “ $\text{Cd}^{2+} - \text{Pb}^{2+} - \text{L} - \text{OH}^- - \text{N}_2\text{H}_4\text{CS}$ ” systems (where $\text{L} - \text{C}_6\text{H}_5\text{O}_7^{3-}$, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $\text{C}_6\text{H}_5\text{O}_7^{3-} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) were calculated by analyzing of the ion equilibrium. Scanning electron microscopy and energy dispersive analysis results showed the effect of the nature and strength of the complexing agents on composition and morphology of synthesized nanocrystalline CdS – PbS films.

Keywords: ionic equilibrium, ligands, hydrochemical deposition, thin films, lead sulfide, cadmium sulfide, substitutional solid solutions.

Introduction

At present, more and more attention to the issues of detecting infrared radiation is given to heterostructures. The use of these materials allows for a more meaningful results compared with the photodetectors based on silicon and germanium. The use of functional-elements on the basis of substitutional solid solutions is also very attractive in this respect. Changing the content of the replacement component we can regulate their properties over a wide range and the range depends on differences of the basic compounds characteristics. In particular, change of cadmium content in composition of the $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ solid solution allows widely varying characteristics of the semiconductor material from the narrow-band galena PbS ($\Delta E_g = 0.41\text{eV}$) to wide- band CdS ($\Delta E_g = 2.4\text{ eV}$). This ensures effective solution of various problems in optoelectronics, such as the manufacture of environmental monitoring instrumentation, optical sensors of temperature control, fast-acting photodetector e.t.c.

However, according to the equilibrium phase diagram [1, 2] sulphides of lead and cadmium don't form a continuous series of solid solutions and their mutual solubility is decreases with the temperature: solubility limit of cadmium sulfide into lead sulfide reaches 38 mol. % at 1325 K and it does not exceed $9 \cdot 10^{-3}$ mol. % at 523 K. Probably the prevalence of high temperature methods of

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preparing solid solutions in the system CdS – PbS [3, 4], requiring complex and expensive technological equipment due to this.

The use of chemical bath deposition method which is related to methods of "light chemistry" (at temperatures below 373 K) for preparing of solid solution allows to expand the range of mutual solubility of the sulfides to form a supersaturated metastable solid solutions and reduce the costs associated with the technical process equipment [5] by the features of colloid-chemical process step [6, 7]. Experimental confirmation of this can be found in Kitaev's and his disciples' works [8-12]. They obtained homogeneous thin films $Cd_xPb_{1-x}S$ with a maximum of replacement share 16.1 mol. % by chemical bath deposition from the reaction mixture containing metal salts, thiourea as halkogeneizator and ligands complexing cadmium and lead ions (sodium citrate and ammonia) [10-12].

It was found [10] that the content of cadmium sulfide in $Cd_xPb_{1-x}S$ solid solution is actually a function of the ratio of lead and cadmium ions concentration in the reaction mixture, i.e. the ratio of rates of the CdS and PbS sulphides formation. Among factors that affect at the rate of synthesis process, a special role in the reaction bath is for ligand background: through the use of the ligands of different strength and nature it can regulate the amount of free metal ions in the solution.

This work is dedicated to the thermodynamic evaluation of the possibility of forming $Cd_xPb_{1-x}S$ films by chemical bath deposition using a same ligands for both metal (citrate ions $C_6H_5O_7^{3-}$, ethylenediamine $H_2NCH_2CH_2NH_2$) and different ligands, in particular, mixtures of ethylenediamine with citrate ions ($C_6H_5O_7^{3-} + H_2NCH_2CH_2NH_2$) and moreover the study of the effect of the ligand background on the films morphology and composition.

Experimental

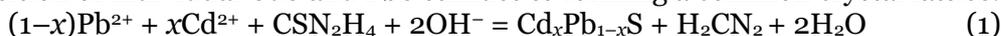
Deposition of films in a system CdS – PbS carried out at a temperature of 358 K for 120 minutes on a degreased sital substrate ST-50. The reaction mixture contained metal salts $Pb(C_2H_3O_2)_2$ (0.04 – 0.068 M) and $CdCl_2$ (0.05M), thiourea CSN_2H_4 (0.6 M) as a source of S^{2-} ions, and various ligands for metal ions. As ligands depending on the system used: sodium citrate $Na_3C_6H_5O_7$, ethylenediamine $H_2NCH_2CH_2NH_2$ and a mixture of ethylenediamine with citrate ion ($H_2NCH_2CH_2NH_2 + C_6H_5O_7^{3-}$).

The film thickness was determined by interference microscopy on the microinterferometer Linnik MII-4M.

Study of the surface morphology and elemental composition of the films was performed by scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (the EDX) using the Scanning Electron Microscope JEOL JSM-5900LV.

Results and discussions

Obtaining of metal sulfides thin films by chemical bath deposition is a complex multi-step process, which is based on the reaction of interaction of the metal ion complexed with sulfide ion, which is formed as a result of thiourea hydrolytic decay [5]. Since S^{2-} ion can potentially be distributed between the two metal ions at the co-precipitation CdS and PbS sulfides, the formation of substitutional solid solution phase in the reaction system takes place in two competing reactions deposition of individual CdS and PbS sulfides to forming a common crystal lattice:



The proportion of the active uncomplexed metal ions that can enter into a chemical reaction with sulfur ions, can be estimated using the expression:

$$\alpha_{Me^{2+}} = \frac{[Me^{2+}]}{C_{Me}} = \frac{1}{1 + \frac{[L]}{k_1} + \frac{[L]^2}{k_{1,2}} + \dots + \frac{[L]^n}{k_{1,2,\dots,n}}} \quad (2)$$

where $[Me^{2+}]$ – concentration of free metal ions; C_{Me} – analytical total concentration of metal ions in the solution; L – ligand concentration; $k_1, k_{1,2}, k_{1,2,\dots,n}$ – instability constants of different metal complex forms.

To determine complex forms prevailing in the solution that exert a decisive influence on the process in each of the systems analysis of the ion equilibrium was held in $Cd^{2+} - L - H_2O$ and $\langle Pb^{2+} - L - H_2O \rangle$ systems was carried out. Contributions of each of the metal ions to the total concentration in the solution can be calculated similarly (2), by substituting in the numerator of

the expression the respective concentration of the complex instead of free cadmium ion concentration.

At choosing synthesis parameters an important factor is apriori estimation of the forming solid solution possibility under certain conditions that can help to reduce an amount of experimental research. That's why in this work thermodynamic calculation of the concentration areas and the pH range of the existence of metal sulfides and impurity phases – hydroxides and cyanamide that were considered due to most of them provide a high level of supersaturation on them in solution because of having a low solubility [5].

The minimum of necessary metal salts concentration was calculated using expression [5]:

$$pC_H = pSP_{MeS} - p\alpha_{Me^{2+}} - \left(pk_{H_2S} - 2pH + 0.5pK_c + p[N_2H_4CS]_H + +0.5p \frac{\beta_C}{\beta_S} \right) - \frac{0.86 \cdot \sigma \cdot V_M}{R \cdot T \cdot r_{cr}}, \quad (3)$$

where C_H – the minimum of required for the the solid phase formation concentration of metal salt; SP_{MeS} – product of metal sulfide solubility ($pSP_{CdS} = 26.10$; $pSP_{PbS} = 27.8$); k_{H_2S} – constant of hydrogen sulphide ionization, that is product of thiourea degradation $pk_{H_2S} = 19.88$; K_c – constant of hydrolytic thiourea degradation $pK_c = 22.48$; $[N_2H_4CS]_H$ – the initial concentration of thiourea; Δ_{cr} – the critical value of supersaturation; σ – specific surface energy of metal sulfide; V_M – molar volume of the synthesized phases; r_{kp} – the radius of the critical size embryo; R – universal gas constant; T – temperature of the process. Values β_S and β_C are equal $\beta_S = [H_3O^+]^2 + k_{HS} \cdot [H_3O^+] + k_{H_2S}$ and $\beta_C = [H_3O^+]^2 + k_{HCN_2} \cdot [H_3O^+] + k_{H_2CN_2}$ [7], where $k_{HS} = (1.0 \cdot 10^{-7})$ and $k_{HCN_2} = (4.7 \cdot 10^{-11})$ – constants of hydrogen sulfide and cyanamide ionization at the first stage; $k_{H_2CN_2} = (3.0 \cdot 10^{-22})$ – constant of cyanamide ionization.

The minimum initial metal salt concentration pC_H that provide formation of phases – $Cd(OH)_2$ and $Pb(OH)_2$ was determined by equation [5]:

$$pC_H = pSP_{Me(OH)_2} - p\alpha_{Me^{2+}} - 2pK_W + 2pH_H, \quad (4)$$

where $pSP_{Cd(OH)_2} = 13.66$ [13]; $pSP_{Pb(OH)_2} = 15.5$ [13]; $pK_W = 14$ [13].

For the calculation of conditions of metal cyanamide formation was used equation [7]:

$$pC_H = pSP_{MeCN_2} - p\alpha_{Me^{2+}} - \left(pk_{H_2CN_2}^{1,2} - 2pH_H + 0.5pK_c + 0.5p[N_2H_4CS]_H + +0.5p \frac{\beta_S}{\beta_H} \right), \quad (5)$$

where $pSP_{CdCN_2} = 14.1$ [14]; $pSP_{PbCN_2} = 15.8$ [14]; $pk_{H_2CN_2}^{1,2} = 21.52$ [13].

Thermodynamic evaluation of the $Cd_xPb_{1-x}S$ solid solution formation conditions at co-precipitation of CdS and PbS sulfides was carried out by a joint solution of equations (3) for lead and cadmium.

In this paper discusses three reaction systems that contain in various set of ligands which are complexed cadmium and lead ions: sodium citrate $Na_3C_6H_5O_7$, ethylenediamine $H_2NCH_2CH_2NH_2$ and a mixture of ethylenediamine with citrate ion ($H_2NCH_2CH_2NH_2 + C_6H_5O_7^{3-}$).

According to the results of ionic equilibria analysis, the influence of hydroxide ions is relatively small until $pH = 13$ in all systems, which is difficult to achieve under the above conditions (Fig. 1-3). When we used citrate ions as a ligand, in almost entire range of pH as lead and cadmium are in solid bound complexes $Pb(OH)Cit^{2-}$ ($pk = 13.7$) and $Cd(OH)Cit^{2-}$ ($pk = 9.3$) (Figure 1a). Indicator of cadmium complex instability constant is significantly lower whereby primarily cadmium sulfide solid phase is formed in a solution (Figure 1b) that can prevent the formation of substitutional solid solution instead of the mixture of the CdS and PbS individual phases.

To solve the problem of solid solution forming it can be the use of an additional ligand for cadmium for which strength complexes with cadmium is better than for complexes with lead. It is known quite a number of works devoted to the preparation of a solid solution $Cd_xPb_{1-x}S$ by chemical bath deposition, where sodium citrate was used as ligands for lead, and ammonia was used as ligands for cadmium [8-10]. In [15] as an alternative to ammonia it is proposed to use ethylenediamine that is less volatile and has ionization constant close to that of ammonia.

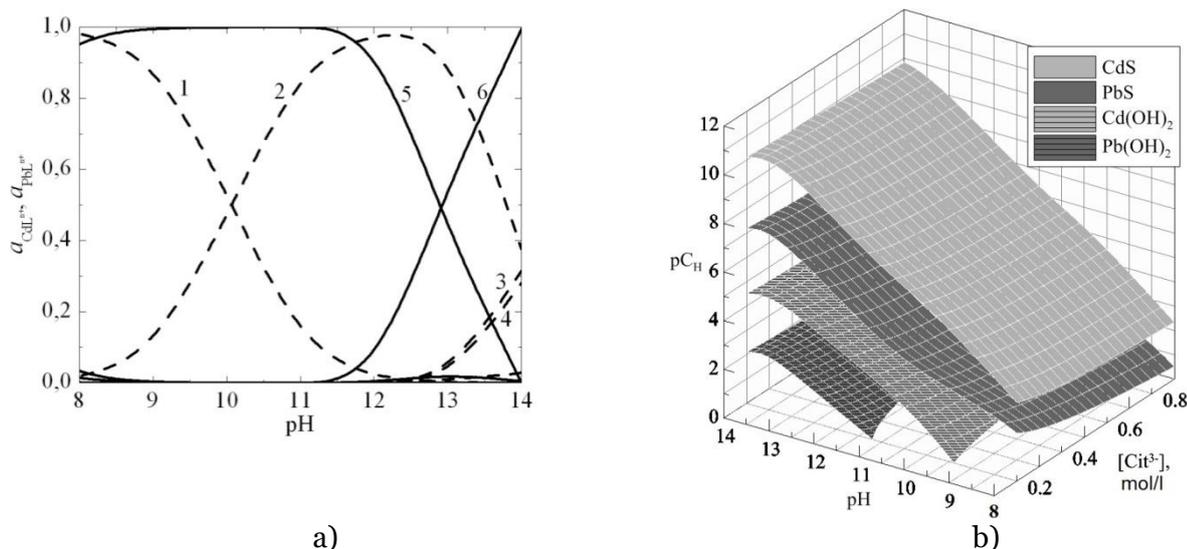


Figure 1. Ionic equilibria in system “Cd²⁺ – Pb²⁺ – Cit³⁻ – H₂O” (a): 1 – CdCit³⁻, 2 – Cd(OH)Cit²⁻, 3 – Cd(OH)₃⁻, 4 – Cd(OH)₄²⁻, 5 – Pb(OH)Cit²⁻, 6 – Pb(OH)₄²⁻; the boundary conditions of CdS, PbS, Cd(OH)₂, Pb(OH)₂ formation in system “Cd²⁺ – Pb²⁺ – Cit³⁻ – N₂H₄CS” taking into account the factor of the crystallization (b). The calculation was performed with [CS(NH₂)₂] = 0.6 mol/l.

According to the ionic equilibrium analysis in the system, where the complexing agent for metals is only ethylenediamine and major complex compounds that prevent rapid precipitation of metal sulfides in the work range of pH = 11-12 [7] for cadmium is Cd(En)₂²⁺ (pk = 10.22) и Cd(En)₃²⁺ (pk = 12.29); for lead Pb(En)₂²⁺ (pk = 8.45) (Figure 2a). There is the opposite situation – the cadmium ions complexed stronger than Pb²⁺ and firstly solids PbS is formed at pH <12.5. At high pH (greater than 13) stable complex Pb(OH)₄²⁻ becomes dominant for the lead. Thus there is the intersection zone of concentration planes of PbS and CdS formation, i.e. at this value of pH (~ 12.5) formation of solid individual sulphide phases occur simultaneously and hence likely formation of a substitution solid solution.

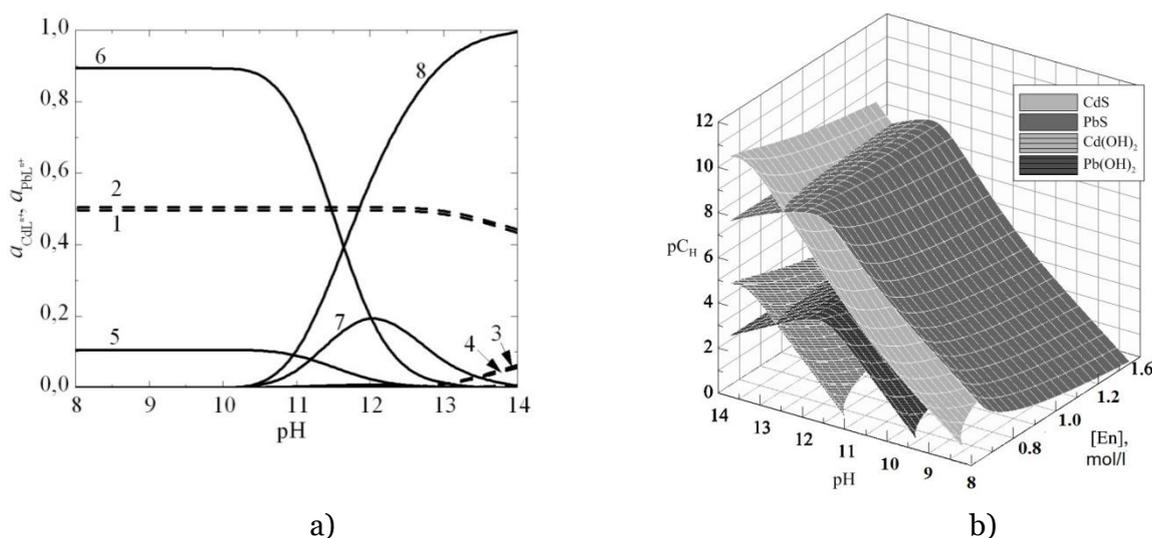


Figure 2. Ionic equilibria in system “Cd²⁺ – Pb²⁺ – En – H₂O” (a): 1 – CdEn₂²⁺, 2 – CdEn₃²⁺, 3 – Cd(OH)₃⁻, 4 – Cd(OH)₄²⁻, 5 – PbEn²⁺, 6 – PbEn₂²⁺, 7 – Pb(OH)₃⁻, 8 – Pb(OH)₄²⁻; the boundary conditions of CdS, PbS, Cd(OH)₂, Pb(OH)₂ formation in system “Cd²⁺ – Pb²⁺ – En – N₂H₄CS” taking into account the factor of the crystallization (b). The calculation was performed with [CS(NH₂)₂] = 0.6 mol/l.

Using specific ligands for each of the metals: citrate ions to lead and ethylenediamine to cadmium (Figure 3) allows to move the intersection of concentration planes in a pH range from 11.5 to 12.5 (Figure 3b). This is due to the fact that the ions Cd^{2+} are bound in ethylenediamine complexes CdEn_2^{2+} ($\text{pk} = 9.98$) and CdEn_3^{2+} ($\text{pk} = 10.21$), which are similar in strength to connecting lead complex Pb(OH)Cit^{2-} ($\text{pk} = 13.7$) (Figure 3a).

As a result, according to preliminary calculations, citrate – ethylenediamine system is the most promising for the production of solid solutions in the system $\text{CdS} - \text{PbS}$ from a thermodynamic point of view.

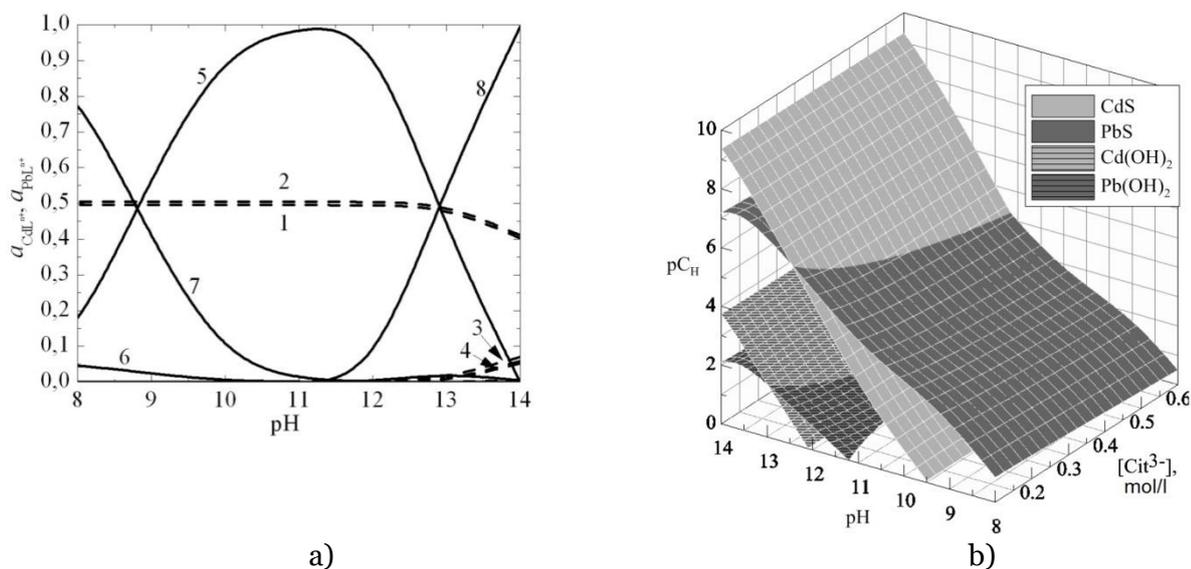


Figure 3. Ionic equilibria in system “ $\text{Cd}^{2+} - \text{Pb}^{2+} - \text{Cit}^{3-} - \text{En} - \text{H}_2\text{O}$ ” (a): 1 – CdEn_2^{2+} , 2 – CdEn_3^{2+} , 3 – Cd(OH)_3^- , 4 – Cd(OH)_4^{2-} , 5 – Pb(OH)Cit^{2-} , 6 – PbEn^{2+} , 7 – PbEn_2^{2+} , 8 – Pb(OH)_4^{2-} ; the boundary conditions of CdS , PbS , Cd(OH)_2 , Pb(OH)_2 formation in system “ $\text{Cd}^{2+} - \text{Pb}^{2+} - \text{Cit}^{3-} - \text{En} - \text{N}_2\text{H}_2\text{CS}$ ” taking into account the factor of the crystallization (b). The calculation was performed with $[\text{CS(NH}_2)_2] = 0.6 \text{ mol/l}$.

It is worth noting that the preliminary calculations of ionic equilibrium in the system “ $\text{Cd}^{2+} - \text{Pb}^{2+} - \text{L} - \text{N}_2\text{H}_4\text{CS}$ ” ($\text{L} - \text{C}_6\text{H}_5\text{O}_7^{3-}$, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $\text{C}_6\text{H}_5\text{O}_7^{3-} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) only indicate the principle possibility of the process chemical bath deposition of lead and cadmium sulfide solid phases, without considering the ways in which they flow. Therefore, in order to prove the correctness of the thermodynamic evaluation and to determine the actual effect of the ligands nature on the formation of a semiconductor $\text{CdS} - \text{PbS}$ there was carried out the synthesis of $\text{CdS} - \text{PbS}$ thin film sample from ethylenediamine and ethylenediamine–citrate. The temperature of synthesis of all systems was 353 K. As a result, the thin films with thickness of about 100 nm evenly covering the substrate were prepared, its surface microimage are shown in Figure 4.

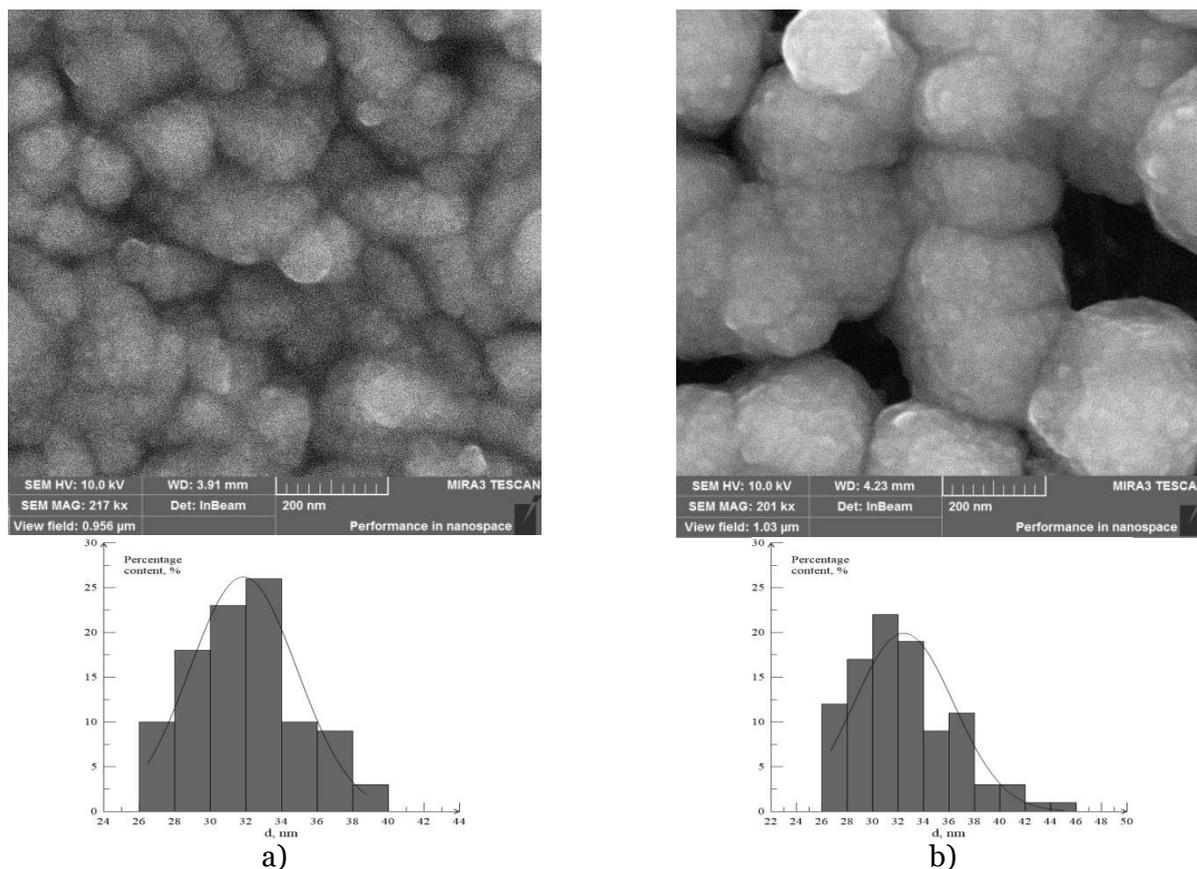


Figure 4. Scanning electron microscopy image of CdS – PbS films that are received at 353 K for 120 minutes by chemical bath deposition of ethylenediamine (a) and citrate – ethylenediamine (b) system at increase of $\times 200\ 000$ and its particle size distribution diagrams

Studies of the films microstructure by scanning electron microscopy and the elemental analysis results indicate about the formation of compounds that contains Cd, Pb, S as major components. Relative sulfur content in all samples was 50 ± 5 at. %. The determination of oxide phases in samples by the elemental analysis was not accurately because of the fact that the total amount of oxygen is submitted by the substrate material due to the small thickness of the films. In this regard, the presence of oxygen in the films are not taken into account.

Samples obtained from the reaction systems containing a different set of ligands are differ from each other both in the composition (Table 1) and layer morphology (Figure 4). The films of ethylenediamine system are characterized by the most uniform surface, that consist of spherical particles of about 25–35 nm united in globules of 180-200 nm densely covering the surface of the substrate. This indicates that in this system both metals are bound in complexes stronger and influence of ligand on the proportion of free ions Cd^{2+} and Pb^{2+} is approximately the same. This is confirmed by the composition film samples: ratio of this metals is close to one (28.8 at. % lead and 20.7 at.% of cadmium).

The cadmium content in the films made from the citrate-ethylenediamine system greatly exceeds the lead content (see Table 1), based on what it can be assume that $\text{Pb}(\text{OH})\text{Cit}^{2-}$ complexes that are characterized by high constant of ionization ($\text{pk}(\text{Pb}(\text{OH})\text{Cit}^{2-}) = 13.7$), reduce the proportion of free ions of lead, cadmium in turn is connected to ethylenediamine complexes. The particles that form the surface of CdS film in citrate – ethylenediamine system which have the same size are combined into larger agglomerate of ~ 350 nm compared with the previous system and its amount is significantly lower, whereby they are less tightly adjacent to each other (Figure 5b.)

Table 1. The elemental composition of the CdS - PbS films, obtained by Chemical bath deposition in systems with different ligand background

Ligands	Content of elements sat. %		
	Pb	Cd	S
H ₂ NCH ₂ CH ₂ NH ₂	28.8	20.7	50.5
C ₆ H ₅ O ₇ ³⁻ + H ₂ NCH ₂ CH ₂ NH ₂	5.8	39.5	44.65

The reasons of differences in the morphology of films in systems with different ligand background are ambiguous because of chemical bath deposition is a complex process and the ligand molecules may influence on the formation of films, both at the stage of nucleation due to the strength of the resulting metal complex forms, and at the stage of film growth due to different spatial structures ligand molecules [19].

Conclusions

In this work the analysis of ionic equilibrium in reaction systems «Cd²⁺ – L – CS(NH₂)₂» and «Pb²⁺ – L – CS(NH₂)₂», where L – C₆H₅O₇³⁻, H₂NCH₂CH₂NH₂, (C₆H₅O₇³⁻+H₂NCH₂CH₂NH₂) was carried out. The ranges of pH and minimum concentrations of metal salts that are necessary for the formation of solid phases of lead and cadmium sulfide, as well as impurity related compounds – metals hydroxides and cyanamides were identified. The thermodynamic probability of solid solutions CdS – PbS formation in these systems were shown.

Thin film samples with good adhesion to the substrate from ethylenediamine, ethylenediamine, ethylenediamine-citrate and triethanolamine systems were prepared by chemical bath deposition, its thickness was about 100 nm.

The studies of scanning electron microscopy of the films CdS – PbS shows nanocrystal character of their surface.

The results of EDX-analysis of the film showed that the composition of the samples depends essentially on the ligand background that is produced in the reaction mixture. Thus, the ratio of metals in the ethylenediamine system is close to one, whereas in the films of the citrate-ethylenediamine systems cadmium content is much more as compared with lead.

Acknowledgements

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