Influence of the Ligand Nature on the Boundary Conditions of the Formation and the Morphology of Nanocrystalline Cadmium Sulfide Films

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Abstract—Ionic equilibriums in the Cd^{2+}–L–N_2H_4CS (L = NH_3, $H_2NCH_2CH_2NH_2$, $C_6H_5O_7^{3-}$, $NH_3 + C_6H_5O_7^{3-}$) systems have been analyzed. The ranges and boundary conditions of the formation of cadmium sulfide CdS and the accompanying $Cd(OH)_2$ and $CdCN_2$ impurity phases have been determined. 100–200 nm thick nanocrystalline cadmium sulfide films constituted by 10–30-nm particles arranged into globules with diameter of 400–700 nm have been synthesized. The effects of the nature and strength of the complexing agent on the microstructure and morphology of the resultant CdS layers have been demonstrated using scanning electron microscopy.

Keywords: hydrochemical synthesis, ionic equilibrium, thin film, cadmium sulfide, surface morphology

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Cadmium sulfide is among the most popular materials finding various applications in semiconductor opto- and nanoelectronics. Polycrystalline thin films on its basis have been used for manufacturing photodetectors and luminescent screens, quantum dots, and sensor elements. There has been a continuous interest in cadmium sulfide application in high-performance solar radiation converters [1].

Among techniques used to prepare thin films of cadmium sulfide, the chemical bath deposition (CBD) method [2–4] is worthy of special mention because of easy implementation requiring no sophisticated equipment as well as high quality and reproducible properties of the so produced coatings.

As far as the mechanism is concerned, the preparation of cadmium sulfide films via hydrochemical deposition involves a set of complex intermolecular interactions between the metal ionic species, various ligands, and the chalcogenizer in the system volume and at the substrate surface. This process can be generally described by Eq. (1), with L being the molecular form of the ligand.

$$CdL_x^{2+} + N_2H_4CS + 4OH^- = CdS\downarrow + xL + CN_2^{2-} + 4H_2O. \quad (1)$$

The metal binding into a complex aims to slow down the sulfide deposition process in order to produce CdS crystallites and film in the reaction system. It is therefore naturally to presumed that changing the ligand strength, concentration, and degree of the spatial structure development should affect the rate and mechanism of the process due to changes in the amount of the free metal ions, thus allowing for the process control and preparation of the samples with the required surface parameters.

Most studies dedicated to the preparation of cadmium sulfide thin films via the hydrochemical deposition have employed ammonia as the binding agent for the Cd^{2+} ions [5–7]. However, a comprehensive physico-chemical approach to hydrochemical deposition of cadmium sulfide has been lacking in these papers; consequently, no reasons for choosing a specific formulation and its composition have been given.

Optimization of the process parameters of the thin films hydrochemical deposition (in particular, the

reaction mixture composition) can be simplified by preliminary analysis of the ionic equilibriums in the system and calculation of the concentration and pH ranges of existence of the metal sulfide. The corresponding procedure has been detailed in [8] and successfully verified by us earlier [9–11].

This study aimed to correlate the morphology of the cadmium sulfide thin film surface and the conditions created in the reaction mixture volume by the ligand background. In particular, we considered four reaction systems for the deposition of cadmium sulfide films, containing the following species capable of cadmium ions complexing: citrate ions, ethylenediamine, ammonia, and an ammonia–citrate mixture.

In the first approximation, the criterion of the cadmium sulfide formation in dilute solutions via reaction (1) is expressed by condition (2), i.e. the ionic product IP_{Cds} (the product of the activities of the free forms of the metal ion Cd^{2+} and of the chalcogenide ion S^{2-}) should exceed the solubility product of the CdS solid phase SP_{Cds} (constant at a given temperature).

$$IP_{Cds} \geq SP_{Cds}. \qquad (2)$$

The excess surface energy of the nuclei appearing upon formation of stable centers of condensation of a new phase should be compensated by certain supersaturation with respect to cadmium sulfide. The supersaturation is defined as the excess of the ionic product over the solubility product; in the case of cadmium sulfide it can be expressed using Eq. (3).

$$\Delta = \frac{IP_{Cds}}{SP_{Cds}}. \qquad (3)$$

It should be noted that the supersaturation created in the system depends on the concentration of the free cadmium ions in the reaction mixture volume; it will determine the deposition rate and the formation features of the solid phase as well.

The fraction of the free (active) cadmium ions capable of interaction with sulfide ions can be estimated using expression (4) [13].

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{c_{Cd}} = \frac{1}{1 + \dfrac{[L_1]}{k_1} + \dfrac{[L_2]}{k_{1,2}} + \cdots \dfrac{[L_1]^n}{k_{1,2\ldots n}}}, \qquad (4)$$

with c_{Cd}, the total analytical concentration of the cadmium in the solution; [L], concentration of the free

ligand; k_1, $k_{1,2}$, and $k_{1,2\ldots n}$, instability constants of corresponding complex metal ions.

In this work we used the following values for the instability constants of the complex cadmium ions [12]: $pk_1 = 2.51$ for the mononuclear citrate complex; $pk_2 = 9.3$ for the mixed hydroxide-citrate complex; $pk_3 = 5.41$, $pk_4 = 9.98$, and $pk_5 = 10.21$ for the ethylenediamine complexes; and $pk_6 = 2.51$, $pk_7 = 4.47$, $pk_8 = 5.77$, $pk_9 = 6.56$, $pk_{10} = 6.26$, and $pk_{11} = 4.56$ for the complexes with ammonia.

To determine the dominant complex species in solution giving the major impact on the process rate, we analyzed the ionic equilibria in the $CdCl_2$–ligand–H_2O system in the presence of citrate ions, ethylene-diamine, ammonia, or ammonia–citrate mixture as ligands. The contribution from each of the complexes present in the solution into the total metal con-centration could be calculated via Eq. (4) by substituting the free cadmium ions concentration in the numerator with that of the corresponding complex.

The calculated partial concentrations of the considered complex cadmium species in the aqueous solutions are plotted as a function of pH in Fig. 1.

Analysis of the ionic equilibriums revealed that the fraction of the cadmium hydroxo complexes was very low (0.01–0.2) at pH > 13 in the cases of citrate ions, ammonia, and ammonia–citrate mixture as ligands. With ethylenediamine as the complexing agent, the fraction of the resulting hydroxo complexes increased to 0.35 at pH of 13 to 14. The prevailing complexes preventing rapid precipitation of cadmium sulfide in the $CdCl_2$–ligand–N_2H_4CS system at pH = 13 (the conditions favorable for thiourea decomposition) were $Cd(OH)Cit^{2-}$ (Fig. 1a), $CdEn_2^{2+}$ (Fig. 1b), and $Cd(NH_3)_5^{2+}$ (Figs. 1c and 1d).

Along with metal sulfide, impurity phases of the metal cyanamide and hydroxide could be formed in the reaction mixture. Their content should be taken into account, since most of those phases are poorly soluble and exhibit high levels of supersaturation in solution. To determine the concentration ranges of existence of cadmium sulfide and the mentioned impurity phases in the examined systems, we calculated the boundary conditions of their formation basing on the analysis of the ionic equilibriums. In particular, we utilized the concept of the reversible hydrolytic degradation of thiourea into hydrogen sulfide and cyanamide [14]. The minimum concentration of the cadmium salt required for the formation of the CdS solid phase in the
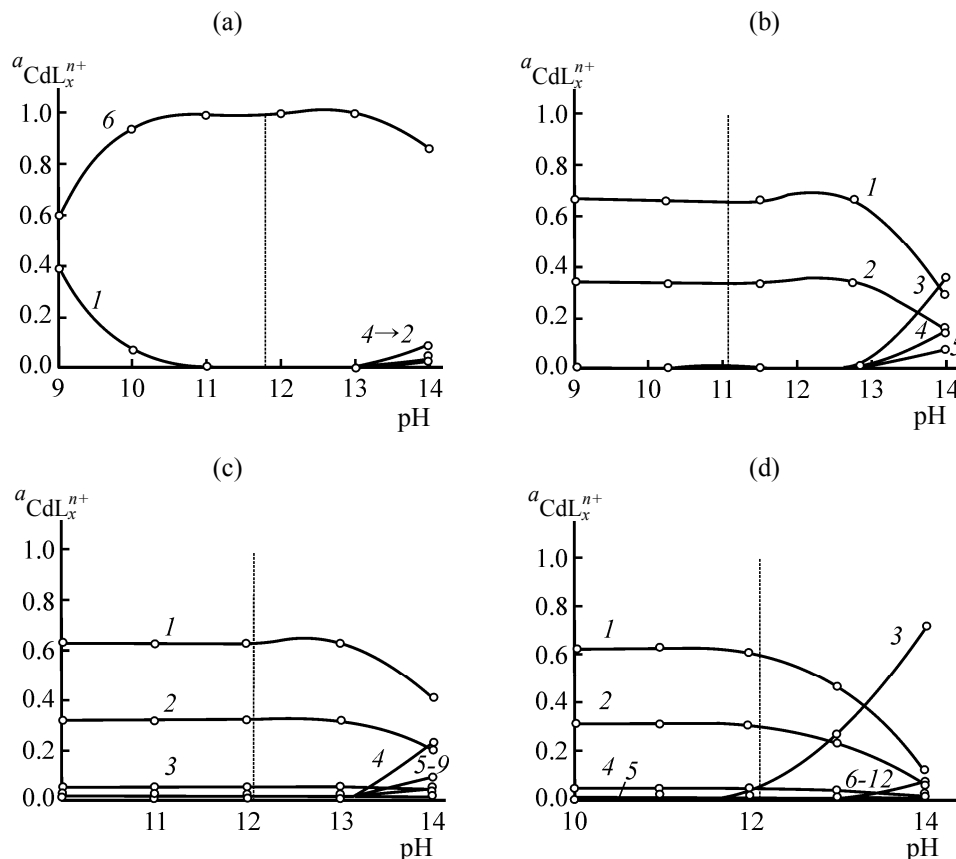
Fig. 1. Calculation of the ionic equilibria in the cadmium salt–ligand reaction systems with (a) citrate ions, (b) ethylenediamine, (c) ammonia, and (d) ammonia-citrate mixture used as ligands. (Dashed line) represents the pH value of the solutions in the systems used. (a): (*1*) $CdCit^+$, (*2*) $CdOH^+$, (*3*) $Cd(OH)_2$, (*4*) $Cd(OH)_3^-$, (*5*) $Cd(OH)_4^{2-}$, and (*6*) $CdOHCit$; (b): (*1*) $CdEn_2$, (*2*) $CdEn_3$, (*3*) $Cd(OH)_3^-$, (*4*) $Cd(OH)_4^{2-}$, and (*5*) $Cd(OH)_2$; (c): (*1*) $Cd(NH_3)_5^{2+}$, (*2*) $Cd(NH_3)_4^{2+}$, (*3*) $Cd(NH_3)_6^{2+}$, (*4*) $Cd(OH)_3^-$, (*5*) $Cd(OH)_4^{2-}$, (*6*) $Cd(OH)_2$, (*7*) $CdNH_3^{2+}$, (*8*) $Cd(NH_3)_2^{2+}$, and (*9*) $CdOH^+$; and (d): (*1*) $Cd(NH_3)_5^{2+}$, (*2*) $Cd(NH_3)_4^{2+}$, (*3*) $CdOHCit$, (*4*) $Cd(NH_3)_6^{2+}$, (*5*) $Cd(OH)_3^-$, (*6*) $Cd(OH)_4^{2-}$, (*7*) $CdCit^+$, (*8*) $CdNH_3^{2+}$, (*9*) $Cd(NH_3)_2^{2+}$, (*10*) $Cd(NH_3)_3^{2+}$, (*11*) $CdOH^+$, and (*12*) $Cd(OH)_2$.

presence of various complexing ions (c_H) was determined using expression (5) [15].

$$\text{p}c_H = \text{pSP}_{Cds} - \text{p}\alpha_{Cd2+} - \{\text{p}k(H_2S) - 2\text{pH} + 0.5\text{p}K_c$$
$$+ \text{p}[N_2H_4CS]_{in} + 0.5\text{p}(\beta_c/\beta_S)\} - (0.86\sigma V_m/RTr_{cr}), \quad (5)$$

with SP_{CdS}, solubility product of cadmium sulfide ($\text{pSP}_{CdS} = 26.10$ [12]); α_{Cd2+}, fraction of the free metal ions; $k(H_2S)$, ionization constant of hydrogen sulfide, one of the thiourea decomposition products $\{\text{p}k(H_2S) = 19.88$ [12]$\}$; K_c, constant of the hydrolytic decomposition of thiourea ($\text{p}K_c = 22.48$ [12]); $[N_2H_4CS]_{in}$, initial concentration of thiourea in the solution; σ, specific surface energy of cadmium sulfide (0.9 J m^{-2}); V_m, molar volume of cadmium sulfide, m^3 mol^{-1}; r_{cr}, radius of the critical nucleus, m; R, universal gas constant, 8.314 J mol^{-1} K^{-1}; and T, temperature of the process, K.

The last term in expression (5) was derived from the Thomson–Ostwald relationship determining the supersaturation level in the system accounting for the formation of the nuclei of the critical size.

The boundary conditions of the formation of cadmium cyanamide were determined using Eq. (6) [15].

$$\text{p}c_H = \text{pSP}(CdN_2) - \text{p}\alpha_{Cd2+} - \{\text{p}k^{1,2}(H_2CN_2) - 2\text{pH}_{in} + 0.5\text{p}K_c$$
$$+ 0.5\text{p}[N_2H_4CS]_{in} + 0.5\text{p}(\beta_S/\beta_c)\}, \quad (6)$$

with $\text{SP}(CdN_2)$, the solubility product of cadmium cyanamide $\{\text{pSP}(CdCN_2)$ 14.1 [12]$\}$; $k^{1,2}(H_2CN_2)$, overall rate constant of the two-stage cyanamide decomposition $\{k^{1,2}(H_2CN_2)$ 21.52 [12]$\}$.

The minimum initial concentration of the cadmium salt $\text{p}c_{in}$ required for the formation of the cadmium hydroxide phase was determined using Eq. (7) [15].
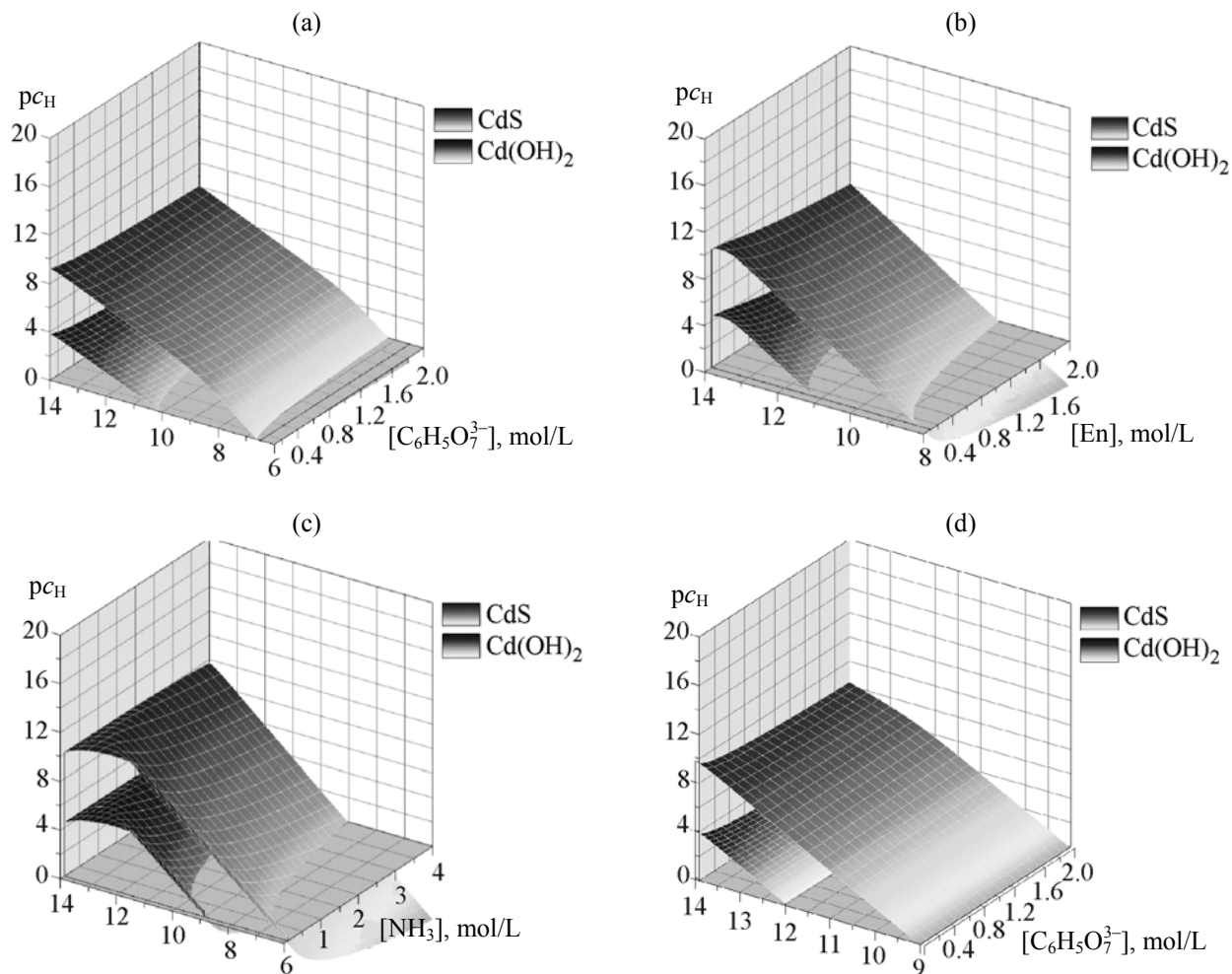
Fig. 2. The boundary conditions of the formation of cadmium sulfide and hydroxide from the CdCl$_2$–ligand–N$_2$H$_4$CS system with (a) citrate ions, (b) ethylenediamine, (c) ammonia, and (d) ammonia-citrate mixture used as ligands.

$$pc_H = pSP[Cd(OH)_2] - p\alpha_{Cd^{2+}} - 2pK_w + 2pH_{in}, \qquad (7)$$

with SP[Cd(OH)$_2$], the solubility product of cadmium hydroxide {pSP[Cd(OH)$_2$] 13.66 [12]}; K_w, ionic product of water.

The calculated boundary conditions and the ranges of deposition of cadmium sulfide, cyanamide, and hydroxide for the four studied reaction systems are presented in Fig. 2 as the surfaces in the coordinates of the initial metal salt concentration, concentration of the ligand, and pH of the solution. The results revealed that the CdS solid phase could be formed at pH of 7 to 14 in the citrate (Fig. 2a) and ammonia (Fig. 2c) systems and at pH of 9 to 14 in the ethylenediamine (Fig. 2b) and ammonia–citrate (Fig. 2d) systems. For all the examined systems, increasing the ligand concentration in the reaction mixture resulted in the

increase of the minimum cadmium concentration required for the sulfide formation.

In the case of the non-activated substrates, the films are deposited exclusively under conditions of the metal hydroxide formation, i.e., the Cd(OH)$_2$ phase acts as the natural surface activator, and the OH$^-$ ions serve as the condensation centers [8].

The data in Fig. 2 show that the hydroxide phase is formed at pH > 9 for the ammonia system and at pH ≥ 10 for the citrate system, pH > 11 for the ethylene-diamine system, and pH > 12 for the ammonia–citrate system.

Furthermore, the calculations revealed that the conditions of the cadmium cyanamide phase formation were not fulfilled in the studied reaction mixtures.

According to our calculations, the pH range of 10–13 was the most favorable for deposition of CdS films from the examined reaction mixtures, and increase of the solution alkalinity lowered the required minimum concentration of the cadmium salt in the solution. We used the pH ≈ 11–12 range at the total concentration of the cadmium salt in the reaction mixture of 0.1 mol/L in this study.

The Thomson–Ostwald equation suggests that the critical nucleus size is determined by the supersaturation level in the system: the higher the supersaturation, the lower the Gibbs free energy of the nucleus formation and the smaller the critical nucleus size ensuring further growth of the solid phase. Using Eq. (2), we calculated the supersaturation level created in the reaction systems of interest based on the operating pH values and the concentrations of the reactants used (see the table).

The tabulated data shows that the film formation occurred in highly supersaturated solutions in all the systems examined. Presumably, the cadmium sulfide crystallites formed in the citrate system exhibiting the highest supersaturation (2.19×10^9) should be the smallest and, consequently, the relatively dense film should be formed on the substrate in that system. The supersaturation level for the ethylenediamine system was two orders of magnitude lower (2.19×10^7) compared to the citrate system, suggesting that smaller amount of larger particles should be formed. That would result in longer lifetime of the island structure of the film and, finally, in formation of a looser packed film. The ammonia–citrate and ammonia systems were in between the mentioned systems in terms of the supersaturation with respect to CdS at higher operating alkalinities of the solution.

In the cases of all the four studied systems, the synthesis run at 353 K during 2 h (other conditions were chosen based on the above-described calculations and the preliminary experiments) resulted in the formation of smooth shiny cadmium sulfide films exhibiting good adhesion to the pyroceramic substrate. The deposited layer was lemon–yellow in the case of the citrate system and yellow-orange in the cases of other systems. The thickness of the uniform film covering the substrate surface ranged from 100 to 200 nm.

Morphology and architecture of the prepared films surface were examined taking advantage of scanning electron microscopy. The images of the layers are shown in Fig. 3. The films were significantly different

Calculated supersaturation levels in the reaction mixtures at the operating pH values

Reaction system	pH	Supersaturation level, Δ
Citrate	11.78	2.19×10^9
Ammonia	12.06	3.39×10^8
Ammonia-citrate	12.12	4.47×10^8
Ethylenediamine	11.65	2.19×10^7

but, irrespectively of the utilized reaction system, they consisted of spherical globules that were in turn built of the smaller particles, predominantly of spherical shape characteristic of cadmium sulfide [16, 17]. However, the electron microscopy data was not fully consistent with the expected effect of the supersaturation level on the film microstructure. In detail, the microscopy images confirmed that the most uniform cadmium sulfide film was indeed prepared from the citrate system; it was constituted by nearly monodisperse globules (≈130 nm) tightly bound together to form a densely packed low-porous layer (Fig. 3a). Similarly, a very dense structure was revealed for the CdS film prepared from the ethylenediamine system; it consisted of virtually identical ≈190 nm aggregates (Fig. 3b). However, the supersaturation level was the lowest during preparation of that film. At the same time, the layers formed from the ammonia and ammonia–citrate systems showed very loose arrangement and highly developed surface. For example, the loose film obtained from the ammonia–citrate system (Fig. 3d) was built of the crystallites non-uniform in size; the 10–30 nm spherical primary particles were arranged into globules with the diameter ranging from 400 to 700 nm.

Microstructure of the CdS film obtained from the ammonia system revealed a special shape of the surface layer in the form of a network matrix (Fig. 2c) arising from the orientation ordering of the 50–200 nm long interconnected fibrillar particles. Such surface layer morphology was responsible for the increased looseness, porosity, and specific surface area of the films.

In the view of the obtained results, it is worthy of note that chemical deposition of films from solutions containing relatively weak ligands typically follows the cluster-cluster aggregation mechanism and results the formation of less ordered and more porous structure [18]. It was reasonable to suggest that the morphology features of the films deposited from the
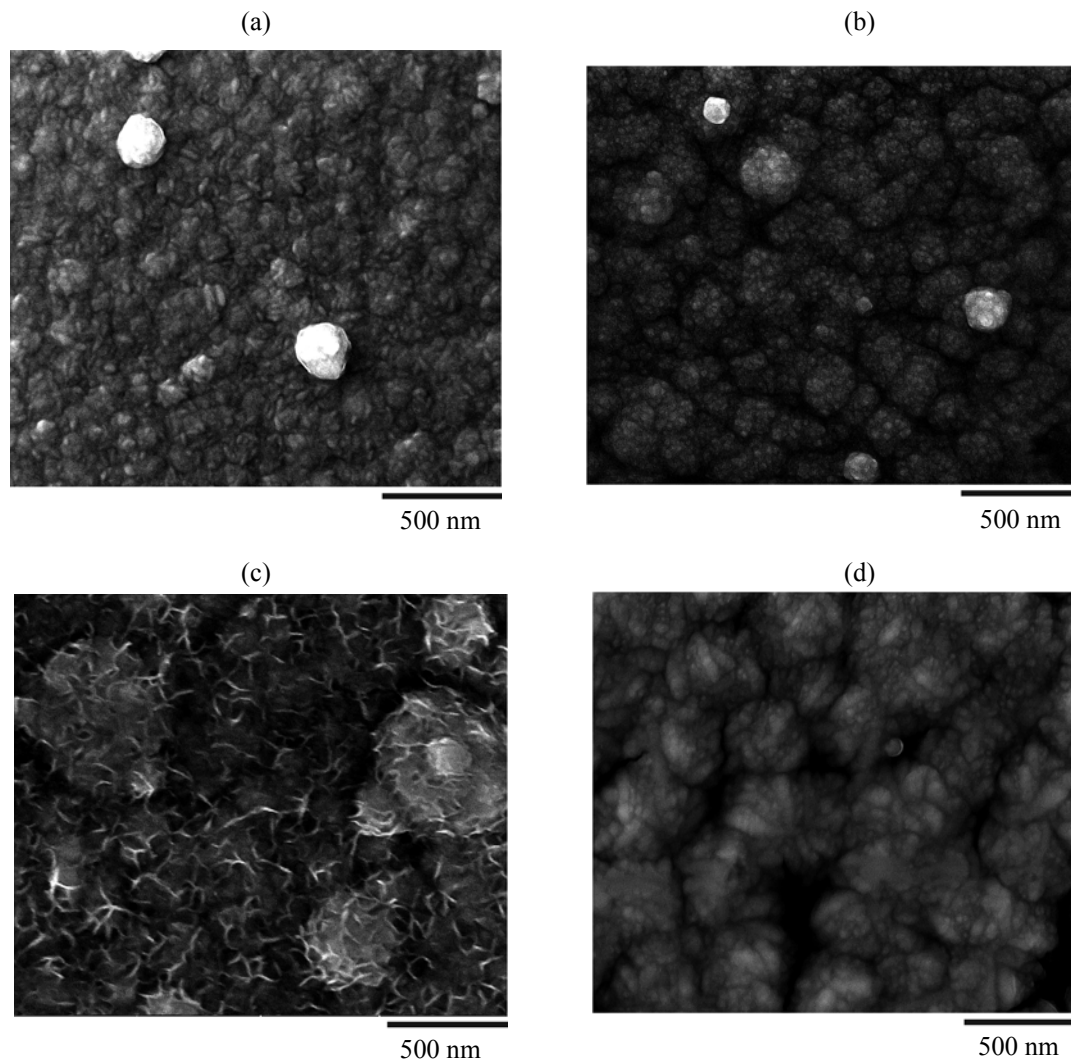
(a)

(b)

500 nm

500 nm

(c)

(d)

500 nm

500 nm

Fig. 3. SEM images of the cadmium sulfide films prepared via hydrochemical deposition from the (a) citrate, (b) ethylenediamine, (c) ammonia, and (d) ammonia-citrate system at 353 K.

ammonia system revealed in this work were largely determined by relatively vigorous formation of the solid phase in the presence of relatively weak ammonia complexes of cadmium in the reaction system.

The fact that the electron microscopy data were not fully consistent with the results of the preliminary calculations was explained as follows. The film formation proceeded in several stages via the different mechanisms including formation of the critical nuclei at the substrate surface, their growth accompanied by intergrowth of the island structures at the substrate, and the film buildup due to the interaction with the dissolved particles or their aggregates subject to Brownian motion in the reaction volume. Hence, the

overall supersaturation level in the system determined only the initial stage of the hydrochemical synthesis, specifically, the nucleation rate. On top of the different complexing ability determining the supersaturation level with respect to the metal sulfide, the ligands used in this work had different spatial structure that could strongly affect the interaction of the primary clusters with the growing CdS film. For example, the adsorbed bulky citrate ions or ethylenediamine molecules could prevent the collisions between the primary clusters in the reaction mixture volume and at the film surface, leading to denser packing of the resulting CdS layers. The smaller ammonia molecule could not provide for the sufficiently strong shielding and therefore did not prevent the particles aggregation.

In summary, we showed that the synthesis of cadmium sulfide films via hydrochemical deposition was a complicated physico-chemical process affected by a number of factors. One of the crucial factors was the ligand background created in the reaction volume. The calcium-binding ligands introduced into the system affected all the growth stages of the cadmium sulfide film formation. The strength of the formed metal complexes and the ligands nature influenced the size and the formation rate of the nuclei appearing at the initial stage of the deposition process as well as the interaction between the primary particles; the latter effect ultimately determined the microstructure and morphology of the prepared films.

EXPERIMENTAL

Thin cadmium sulfide films were prepared via chemical deposition from aqueous solutions of cadmium chloride ("chemical pure" grade) and thiourea ("ultrapure" grade). The alkaline medium promoting the thiourea decomposition was created by addition of ammonia, potassium hydroxide, or ethylenediamine solution, depending on the formulation used. The following additives were used to bind cadmium ions into the complexes and to decelerate the solid CdS phase formation: trisodium citrate ("ultrapure" grade), ethylenediamine ("chemical pure" grade), ammonia ("chemical pure" grade), or a mixture of ammonia with sodium citrate. The cadmium sulfide films were deposited onto preliminarily defatted 30 × 24 mm ST-50-1 pyroceramic substrates. The process was carried out at 353±0.1 K in a TS-TB-10 thermostat.

Structure and morphology of the prepared thin films were examined using a MIRA3LMV scanning electron microscope. The images were taken at acceleration voltage of 10 kV and ×100000 magnification. The films thickness was determined with a Linnik MII-4M interferometer.

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