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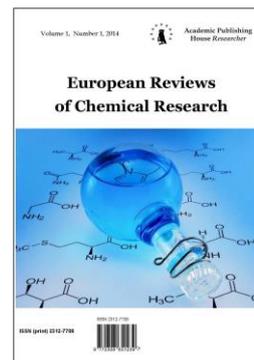
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Kinetic Features of Cadmium Sulfide Deposition from Aqueous Solutions with Various Ligand Backgrounds

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Abstract

A comparative kinetic study was carried out and formal kinetic equations were derived for the chemical deposition of cadmium sulfide from aqueous solutions containing various cadmium complexes onto a glass-ceramic substrate by thiourea under conditions of spontaneous nucleation and interfacial area control. The morphology of the resultant films were examined, on this basis their nanostructure nature was confirmed, taking into account the data on crystallite size analysis.

Keywords: hydrochemical synthesis, cadmium sulfide, chemical kinetics, spontaneous nucleation of solid phase, thin films, surface morphology.

1. Introduction

Cadmium sulfide is the most known direct-bandgap A_2B_6 semiconductor with the forbidden band gap of 2.42 eV, which has for long attracted interest [1]. It has found microelectronic and optoelectronic applications, in particular in light-emitting diodes, lasers, photoelectric converters, solar cells etc. [2–6].

Among the variety of methods used to produce layers for cadmium sulfide-based photovoltaic cells such as vacuum evaporation and condensation in a quasiclosed volume [7], vacuum condensation from a vapor phase [8], pulverization followed by pyrolysis [9] the method of chemical bath deposition of films by thiourea from aqueous solutions of cadmium salts is the most promising [10]. Its attractive features include mild conditions of the preparation of cadmium sulfide layers, low deposition temperature (≤ 353 K), high controllability of the film thickness, and easy modifiability of the film composition and morphology.

Despite the above-mentioned advantages, some technological details of the chemical bath deposition method occasionally hinder the preparation of high-quality cadmium sulfide films, but the functional properties and microstructural characteristics of cadmium sulfide layers should be provided as early as in the hydrochemical synthesis stage.

At the first time hydrochemical deposition of CdS films by thiourea has been studied in the Mokrushin and Tkachev works [11], and the conditions of their formation have been described in

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[12, 13]. The complexing agent for cadmium in those studies was ammonia. More recent studies employed Trilon B [14], ethylenediamine [15], trisodium citrate [16], and amino acids [17] as ligands. Previously, we have performed thermodynamic evaluation of the conditions of formation of solid CdS phase by chemical bath deposition [18]. One of the most important factors influencing the CdS composition and structure is the ligand background created in the reaction system. The stability of the resulting complex metal species and of the spatial structure of the ligand affect both the size of the emerging nuclei and their interactions, which ultimately produce a decisive effect on the micro-structure and morphology of the films synthesized. However, those studies did not report on the rate of formation of the solid phase under conditions of spontaneous nucleation and on the ways of its control with the aim to actively influence the morphology, structure, and electrophysical properties of the deposited films.

As shown in [10], hydrochemical deposition of metal sulfides is a heterogeneous autocatalytic process in which the function of catalyst is fulfilled by the metal sulfide phase formed on the reactor wall surface, on the substrate, or in the reaction mixture volume. Importantly, under conditions of spontaneous nucleation and significant supersaturation the reaction between the sulfidizer and soluble cadmium salt leads to the CdS solid phase formation not only on the substrate surface but also, to a considerable extent, in the reaction mixture volume (as a powdery precipitate).

Here we report about the kinetic features of cadmium sulfide chemical bath deposition by thiourea from solutions with different ligand background under conditions of spontaneous nucleation and control of the solid phase surface area. Kinetic studies aim mainly to identify the role played and contribution made by each component of the reaction mixture to the process rate and to determine how it is affected by the temperature and interfacial area. To this end it is necessary to estimate the partial orders of the CdS formation reaction with respect to all the reactants and the apparent activation energy.

2. Experimental

The reaction mixtures for the hydrochemical deposition were prepared from 2.0 M thiourea (CSN_2H_4 , ultrapure grade), 1.0 M cadmium chloride (CdCl_2 , chemically pure grade), 1.5 M trisodiumcitrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, ultrapure grade), 13 M aqueous ammonia (NH_4OH , chemically pure grade), and 5 M potassium hydroxide KOH, pH of the solutions was monitored with a pH-121 pH-meter.

For the preparation of the reaction mixtures the reactants were mixed in a strictly specified sequence: to a cadmium salt solution the complexing agent was added and next the calculated amount of water, and this was followed by introduction of the alkaline agent (in citrate system) and then of thiourea. The temperature of the stock solutions during the preparation of the reaction mixtures was 293 K. The CdS deposition was carried out in molybdenum glass reactors which were placed in a TS-TB-10 thermostat.

The kinetic research of the cadmium sulfide deposition under spontaneous nucleation conditions over 308–333 K temperature range for three different formulations of the reaction mixture with the total content of cadmium chloride (CdCl_2) and thiourea (CSN_2H_4) of 0.005–0.02 and 0.20–0.60 M, respectively. The first reaction mixture contained citrate ions $\text{C}_6\text{H}_5\text{O}_7^{3-}$ (citrate system), using trisodium citrate Na_3Cit (0.10–0.40 M) as the main complexing agent, the second mixture, aqueous ammonium hydroxide NH_4OH (ammonia system) with concentration 1.0–3.0 M, and the third mixture, both ligands at varied citrate and ammonia concentrations (ammonia-citrate system). For creation of an alkaline medium, KOH was introduced into the citrate reaction bath to pH 11.8; in the two other systems, aqueous ammonium hydroxide whose concentration provided pH from 11.2 to 12.2 served as alkaline agent. The kinetic features of the cadmium sulfide deposition under control of the surface area of the solid phase being formed were studied in the ammonia-citrate system.

The kinetic features of the hydrochemical deposition of the solid phase of cadmium sulfide were studied by the excess concentration method [23]. The changes in the cadmium salt concentration in the reaction mixture were monitored by periodic sampling and analysis of the samples taken by trilonometric back titration using Eriochrome Black T indicator and a buffer solution (pH = 10) [24].

For studying the process kinetics under a controlled interfacial area we used glass powder with an average particle size of 80 μm , previously coated with a chemically deposited cadmium

sulfide layer. The shape of the powder particles was taken as spherical. The surface area contacting the solution was calculated as the sum of the surface area of the reactor walls $S_r = 0.0221 \text{ m}^2$ and the surface area per unit mass of the glass powder $S_{gl.p.} = 0.0305 \text{ m}^2/\text{g}$ which was calculated using the glass powder density (2.45 g/cm^3). The powder particles were kept in suspension by conducting the experiments in a vertically rotating reactor at 10 rpm.

The CdS films were deposited onto $30 \times 24 \text{ mm}$ sital substrates ST-50-1 previously degreased in sulfochromic solution [24]. The thickness of the films deposited was measured by an MII-4M Linnik interferometer.

The initial and final stages of the crystallization of the semiconductor CdS layer were examined by scanning electron microscopy (SEM) using the Scanning Electron Microscope JEOL JSM-5900LV and atomic force microscopy (AFM) using a Ntegra Prima (Russia, NT-MDT) and an Asylum MFP-3D (Asylum, United States) scanning probe microscopes. Scanning was performed in the tapping mode in air at room temperature. The resulting surface images ($1 \times 1 \text{ }\mu\text{m}$ scan area) served for studying the structure of individual globules and for determining the statistical values of the surface parameters, which were quantitatively estimated by computer image processing in Gwyddion program.

3. Results and discussions

The choice of specific concentration and temperature limits in this work was dictated by the results of the preliminary experiments and of the calculations of the CdS formation conditions [18].

Typical kinetic curves of the cadmium sulfide deposition under conditions of spontaneous nucleation of the solid phase from the three reaction systems studied at the initial concentration of the metal salt of 0.01 M and the thiourea concentration of 0.4 M are shown in Figure 1. It is seen that the deposition is characterized by a negligible induction period, with rate that determined by the concentration of the ligands introduced into the reaction mixture. Increase in the ligand concentration in all the systems slows down the conversion of the cadmium salt to CdS. The cadmium sulfide deposition proceeds less intensively in the citrate system: the reaction attains equilibrium within the first 60 min at $[\text{Na}_3\text{Cit}] = 0.1 \text{ M}$ (Fig. 1a, curve 1). The residual concentration of the cadmium ions ($0.55 \cdot 10^{-2} \text{ M}$) increases to $0.7 \cdot 10^{-2} \text{ M}$ under 4-fold increase in the citrate concentration in solution (Fig. 1a, curve 3). This is due to a relatively high stability of the $\text{Cd}(\text{OH})\text{Cit}^{2-}$ complex of cadmium ($\text{p}k_i = 9.3$ [19]). In the ammonia and ammonia-citrate reaction baths (Figs. 1b–1d) the CdS deposition proceeds to lower residual metal concentrations. This can be explained by a lower degree of cadmium complexation by ammonia ($\text{p}k_i$ of the ammonia metal complexes is lower than that of the hydroxycitrate complex) and, on the other hand, by increase in the NH_4OH concentration in solution and in pH, leading to acceleration of the hydrolytic decomposition of thiourea.

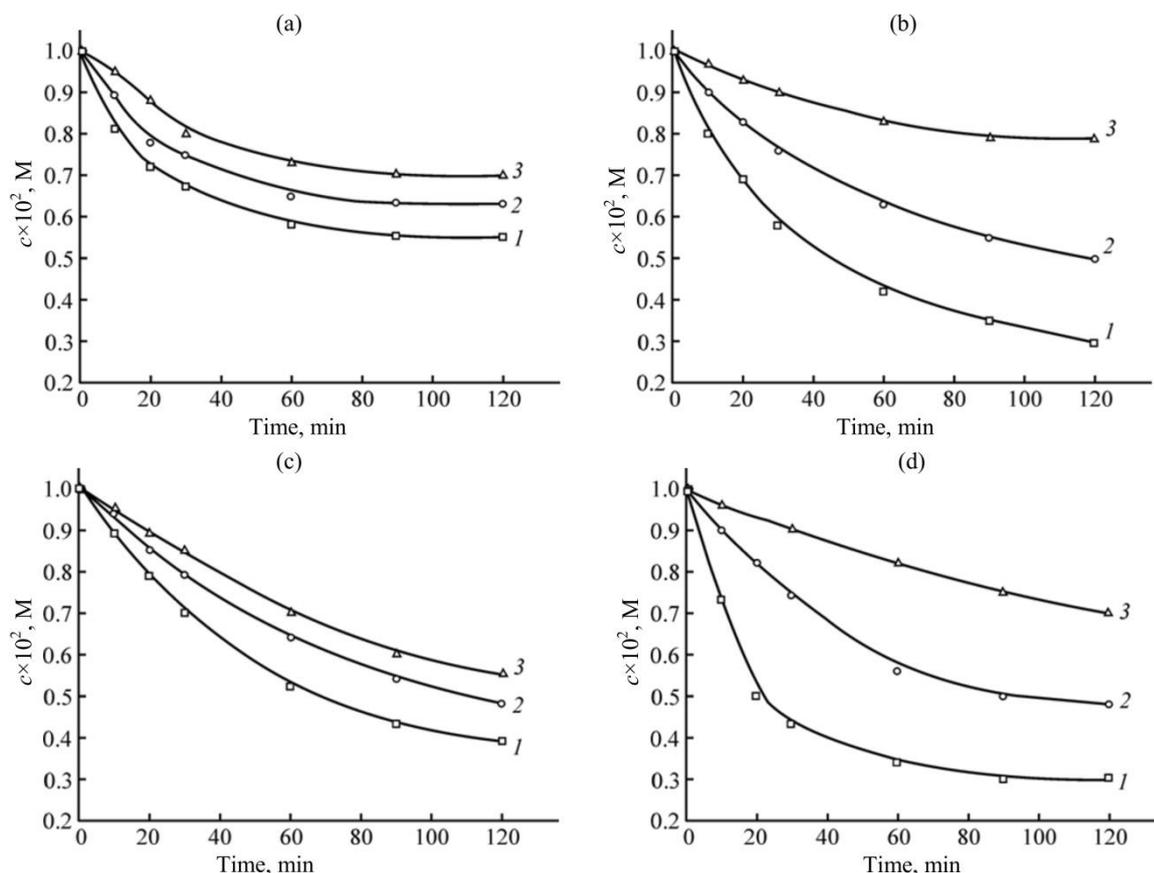


Fig. 1. Kinetic curves of the CdS deposition at 323 K from reaction mixtures of various compositions: (a) citrate, $[\text{Na}_3\text{Cit}]$, M: (1) 0.1, (2) 0.2, and (3) 0.4, (b) ammonia, $[\text{NH}_4\text{OH}]$, M: (1) 2.0, (2) 3.0, and (3) 4.0, and (c, d) ammonia-citrate: (c) $[\text{Na}_3\text{Cit}]$, M: (1) 0.1, (2) 0.2, and (3) 0.4 and $[\text{NH}_4\text{OH}] = 2.0 \text{ M}$ and (d) $[\text{NH}_4\text{OH}]$, M: (1) 1.0, (2) 2.0, and (3) 3.0 and $[\text{Na}_3\text{Cit}] = 0.1 \text{ M}$. Initial CdCl_2 and CSN_2H_4 concentrations, 0.01 and 0.4 M, respectively.

The processing of the experimental data of kinetic in the $\ln C_{\text{Cd}} - \tau$ coordinates revealed the first order with respect to the metal salt concentration for all the reaction systems tested.

Figure 2, for example, presents typical kinetic curves describing the conversion of the cadmium salt to sulfide in the ammonia system in the 303–323 K range. It is seen that the conversion rate is strongly temperature dependent. After 120 min of synthesis at 303 K the residual cadmium concentration in the presence of 0.4 M thiourea and 3.0 M ammonia was ~80% of the initial level, and at 323 K it was 2.7 times lower.

By constructing the Arrhenius plots we determined the activation energies (E_a) of the CdS deposition in different reaction systems and the pre-exponential factors of the equation. Calculated apparent activation energies of cadmium sulfide deposition in the citrate, ammonia, and ammonia-citrate systems and pre-exponential factors are respectively 39.16, 55.25, 63.34 kJ/mol and $1.7 \cdot 10^3$, $2.6 \cdot 10^3$, $1.1 \cdot 10^7$. The E_a data obtained indicate that the process of deposition proceeds in the kinetic regime. It can be assumed that, because of a relatively low energy barrier to nucleation, the deposition in the citrate system will be accompanied by the formation of a large number of primary CdS particles, as predicted earlier by our thermodynamic calculations [18].

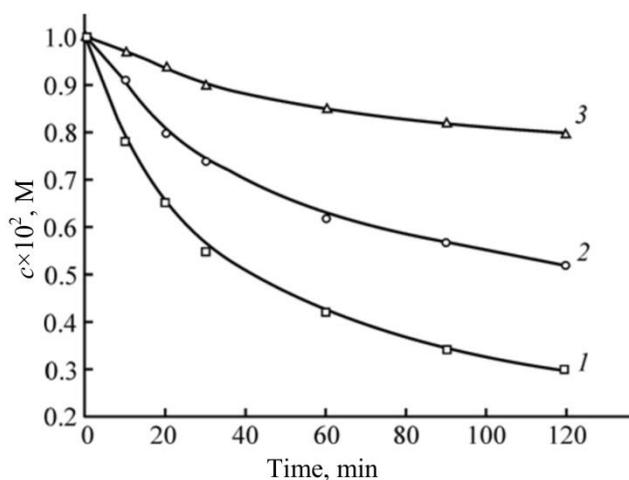


Fig. 2. Kinetic curves of the cadmium salt conversion to CdS at (1) 323, (2) 313, and (3) 303 K. Concentrations of the reactants in the reaction mixture, M: $[\text{CdCl}_2] = 0.01$, $[\text{NH}_4\text{OH}] = 3.0$, $[\text{CS}(\text{NH}_2)_2] = 0.4$.

Using the partial kinetic orders of all reactants, obtained from our kinetic studies, we derived the formal kinetic equations for the conversion of the cadmium salt to CdS solid phase (W_{CdS}) under spontaneous nucleation in all the systems tested. Although not revealing the actual mechanism of the reaction of the cadmium salt with thiourea, eqs. (1) – (3) generally describe the rate of conversion.

$$W_{\text{CdS}(\text{C}_6\text{H}_5\text{O}_7^{3-})} = 1.7 \cdot 10^3 \cdot \exp\left(-\frac{39160}{8.314 \cdot T}\right) \cdot C_{\text{Na}_2\text{Cit}}^{-0.4} \cdot C_{\text{CS}(\text{NH}_2)_2}^{0.7} \cdot (x_\infty - x) \quad (1)$$

$$W_{\text{CdS}(\text{NH}_3)} = 2.6 \cdot 10^3 \cdot \exp\left(-\frac{55250}{8.314 \cdot T}\right) \cdot C_{\text{NH}_3}^{-1.7} \cdot C_{\text{CS}(\text{NH}_2)_2}^{0.3} \cdot (x_\infty - x) \quad (2)$$

$$W_{\text{CdS}(\text{C}_6\text{H}_5\text{O}_7^{3-} + \text{NH}_3)} = 1.1 \cdot 10^7 \cdot \exp\left(-\frac{63340}{8.314 \cdot T}\right) \cdot C_{\text{Na}_2\text{Cit}}^{-0.5} \cdot C_{\text{NH}_3}^{-1.1} \cdot C_{\text{CS}(\text{NH}_2)_2}^{2.0} \cdot (x_\infty - x) \quad (3)$$

Here, x_∞ , x are the cadmium concentrations at the equilibrium established in the reaction mixture (τ_∞) and at any arbitrary time (τ), respectively, and $C_{\text{Na}_2\text{Cit}}$, C_{NH_3} , $C_{\text{CS}(\text{NH}_2)_2}$ are initial concentrations of trisodium citrate, ammonia, and thiourea, respectively.

Equations (1) – (3) and the data calculated show that temperature and thiourea concentration are the most flexible process parameters for controlling the rate of CdS solid phase formation over fairly broad ranges. The effect from an increase in the thiourea concentration in the reaction bath on the cadmium sulfide deposition rate is especially noticeable in the case of the ammonia-citrate system for which the partial order of the reaction with respect to $\text{CS}(\text{NH}_2)_2$ was estimated at 2.0 against 0.7 for the citrate and 0.3 for the ammonia systems. In all cases the ligands produce an inhibitory effect on the CdS formation as indicated by the negative partial kinetic orders.

A nontrivial, in our opinion, route consists in the CdS solid phase deposition onto a known surface area (under surface area control). Here, this was achieved by introducing into the reactor of a strictly measured weighed portion of the glass powder classified into a size group with an average particle size of 80 μm , previously coated with cadmium sulfide. With this technique the probability of spontaneous nucleation of the solid phase in the solution volume is negligible and the process is localized on the powder particles introduced into the solution. The surface area increases insignificantly due to the sulfide film growth on the powder particles, and the catalytic surface area in the course of the experiment is virtually constant.

Figure 3 shows the kinetic curves describing how the cadmium salt concentration in the ammonia-citrate reaction mixture changes upon introduction of 3, 6, and 10 g of the classified glass powder coated with a CdS film. For comparison, 6 g of the glass powder without predeposited cadmium sulfide layer was introduced into solution. At the surface area of the reactor walls of 0.0221 m^2 and the per unit mass surface area of the glass powder of 0.0305 m^2/g the interfacial area was estimated at 0.1136, 0.2051, and 0.3271 m^2 , respectively. In the last case the spontaneous nucleation of the solid phase in the solution volume was negligible and the process was localized on the surface of the powder particles coated with CdS.

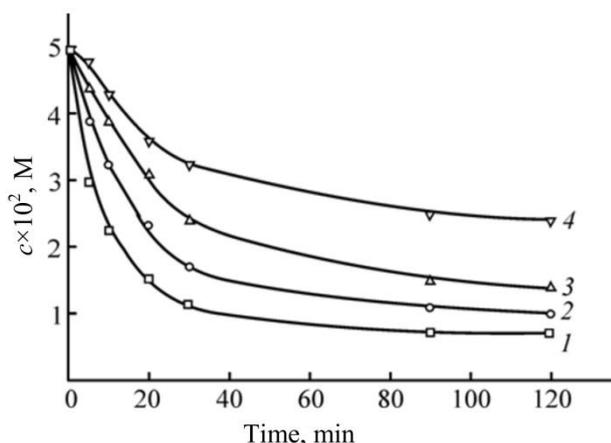


Fig. 3. Kinetic curves of the cadmium salt conversion to CdS upon introduction into the reaction mixture of (4) 6 g of classified glass powder and (3–1): (3) 3, (2) 6, and (1) 10 g of the glass powder previously coated with CdS. Concentrations of the reactants in the reaction mixture, M: $[\text{CdCl}_2] = 0.005$, $[\text{NH}_4\text{OH}] = 3.0$, $[\text{Na}_3\text{Cit}] = 0.1$, $[\text{CS}(\text{NH}_2)_2] = 0.4$; $T = 318 \text{ K}$.

As seen from Fig. 3, in the presence of the glass powder previously coated with a cadmium sulfide film the deposition proceeds more intensively (curve 2) than in the presence of an identical amount of pure glass powder (curve 4). An increase in the weighed portion of the powder sample introduced in the glass reactor from 3 to 10 g causes a proportional increase in the CdS deposition rate (curves 1–3). These findings confirm the autocatalytic nature of the chemical bath deposition of cadmium sulfide by thiourea and demonstrate an expressed dependence of the CdS deposition rate on the interfacial area.

Using the results of the complex kinetic studies on CdS deposition in the ammonia-citrate system with interfacial area (S) controlled by introduction of the glass powder coated with a cadmium sulfide film into the reactor we derived formal kinetic equation linking the cadmium sulfide formation rate W_{CdS} with the deposition conditions:

$$W_{\text{CdS}}(\text{C}_6\text{H}_5\text{O}_7^{3-} + \text{NH}_2) = 6.6 \cdot 10^3 \cdot \exp\left(-\frac{47870}{8.314T}\right) \cdot S \cdot C_{\text{Na}_3\text{Cit}}^{-0.8} \cdot C_{\text{NH}_3}^{-1.3} \cdot C_{\text{CS}(\text{NH}_2)_2}^{0.2} (x_\infty - x) \quad (4)$$

In the presence of cadmium sulfide on the glass powder with a controlled interfacial area the apparent activation energy of the CdS formation is by a factor of 1.3 lower than that under spontaneous nucleation conditions; E_a is 47.87 kJ/mol in this case.

Equation (4) shows that the partial kinetic order with respect to thiourea is by an order of magnitude lower than that obtained with the use of formal-kinetic Eq. (3) derived for spontaneous nucleation conditions, while the partial orders for trisodium citrate and ammonia are close. Testing this equation showed a good agreement between the experimental and calculated data. Thus, by varying the interfacial area during the CdS deposition from aqueous thiourea solutions in vitro it is possible to completely suppress the process in the reactor volume and to redistribute the sulfide phase onto the surface of the substrate introduced.

As noted above, under conditions of spontaneous nucleation of solid phase, cadmium sulfide is deposited both as a precipitate in the solution volume and as a thin film on a substrate placed in solution. Figure 4 illustrates how the CdS layer thickness varies with the deposition time in the ammonia (1), ammonia-citrate (2), and citrate (3) systems.

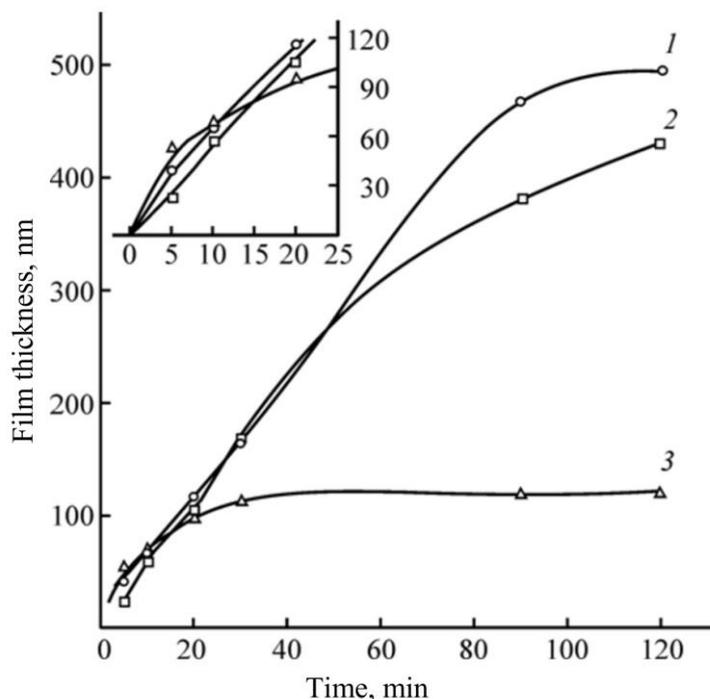


Fig. 4. CdS film thickness as a function of the deposition time in (1) ammonia, (2) ammonia-citrate, and (3) citrate systems. Concentrations of the reactants in the reaction mixture, M: $[\text{CdCl}_2] = 0.02$, $[\text{Na}_3\text{Cit}] = 0.3$, $[\text{NH}_4\text{OH}] = 2.0$, $[\text{CSN}_2\text{H}_4] = 0.4$; $T = 333 \text{ K}$; glass-ceramic substrate. The inset shows the initial period of deposition.

Earlier, we determined the supersaturation level with respect to CdS in the systems examined [18]. The inset in Fig. 4 shows that, in the citrate system, the observed cadmium sulfide film growth in the first minutes somewhat outruns that in the ammonia and ammonia-citrate reaction systems due to a higher supersaturation level ($2.19 \cdot 10^9$ against $3.39 \cdot 10^8$ and $4.47 \cdot 10^8$, respectively [18]).

Figure 5 shows the SEM images of the CdS films formed on the sital substrate 5 min after the beginning of deposition. The film deposited from the citrate system exhibits a relatively high density and the most uniform size distribution of the cadmium sulfide nanoparticles (Fig. 5a). Specifically in this system the nuclei emerge almost instant at the same time over the entire substrate surface (explosive nucleation) due to significant supersaturation with respect to cadmium sulfide ($2.19 \cdot 10^9$) in the first 5 min. In the initial stage of the synthesis the sital substrate surface gets covered with an even layer of 20 – 25 nm CdS particles. The film growth in the citrate system is decelerated after the first 20 min of the process, and after 2 h of synthesis its thickness does not exceed 100 nm (Fig. 4). This can be explained by the fact that, in the course of the fast phase formation reaction under high supersaturation conditions, the emergence of CdS nuclei and their growth are redistributed to the solution volume, consequently reducing the probability of the particle adherence to the substrate [20, 21]. The situation is further complicated by kinetic difficulties, in particular, by the attainment of equilibrium by the reaction system (Fig. 1a).

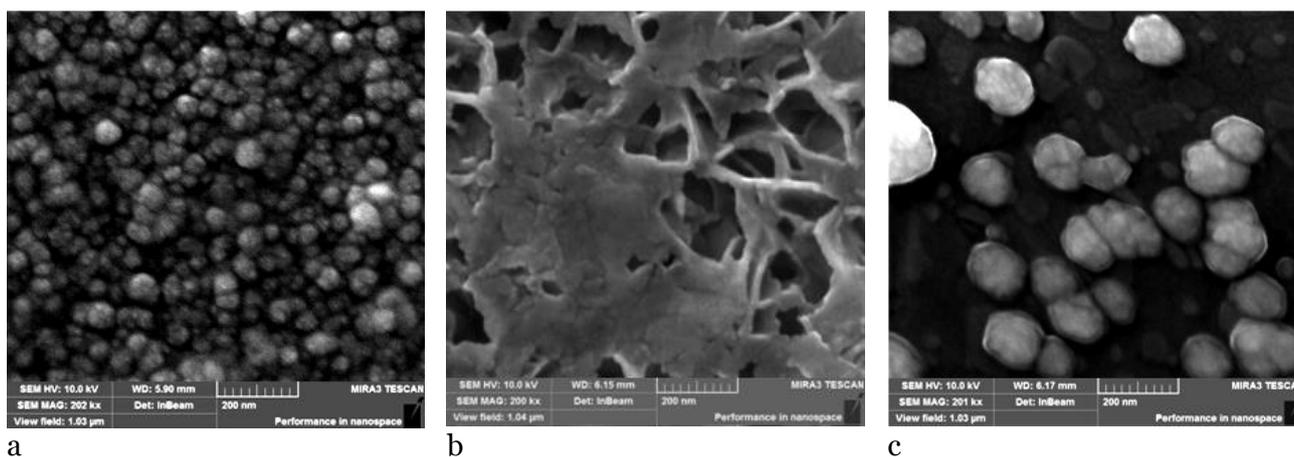


Fig. 5. SEM images of the CdS layers and their 3D representations 5 min after the onset of the deposition from (a) citrate, (b) ammonia, and (c) ammonia-citrate systems. Concentrations of reactants in the reaction mixture, M: $[\text{CdCl}_2] = 0.02$, $[\text{Na}_3\text{Cit}] = 0.3$, $[\text{NH}_4\text{OH}] = 2.0$, $[\text{CSN}_2\text{H}_4] = 0.4$; $T = 333 \text{ K}$.

The supersaturation with respect to cadmium sulfide in the ammonia and ammonia-citrate systems was estimated at $3.39 \cdot 10^8$ and $4.47 \cdot 10^8$, respectively. In the ammonia system (Fig. 5b) the cadmium sulfide film fully covers the substrate surface within 5 min, forming a continuous layer of oblong particles measuring $\sim 80 \text{ nm}$ on the average. The films deposited from the ammonia bath are the thickest among those deposited from the systems considered ($\sim 490 \text{ nm}$ after 2 h of synthesis). In the case of the ammonia-citrate system (Fig. 5c) the CdS film is comprised of $\sim 55\text{-nm}$ particles forming aggregates with sizes up to 200 nm during the synthesis. Large particles formed in small amounts at the initial time. The CdS film deposited onto the sital substrate from the ammonia-citrate bath is slightly thinner ($\sim 430 \text{ nm}$) compared to that deposited from the ammonia system, which is consistent with the kinetic curves describing the conversion of the cadmium salt to sulfide (Fig. 1).

In the case of CdS film nucleation under relatively high supersaturation the island phase density and the substrate filling degree is high. When the production of larger crystallites is required, or the energetically most favorable orientation of the film islands, the super-saturation level should be reduced, but the process may take longer time.

Figure 6 shows the 3D images of the most typical fragments of the surface of cadmium sulfide ($1 \times 1 \mu\text{m}$) deposited within 120 min at 333 K from the reaction mixtures with the use of citrate ions, ammonia, and a mixture of citrate ions with ammonia as complexing agents. The inhomogeneity of the nanocrystalline CdS film surface within the scan was characterized by the arithmetic roughness R_a determining the average deviation of all the points of the roughness profile from the center line. For the cadmium sulfide films deposited from the reaction systems of interest this parameter within the scan increases from 7.9 for the citrate to 45.7 nm for the ammonia-citrate system.

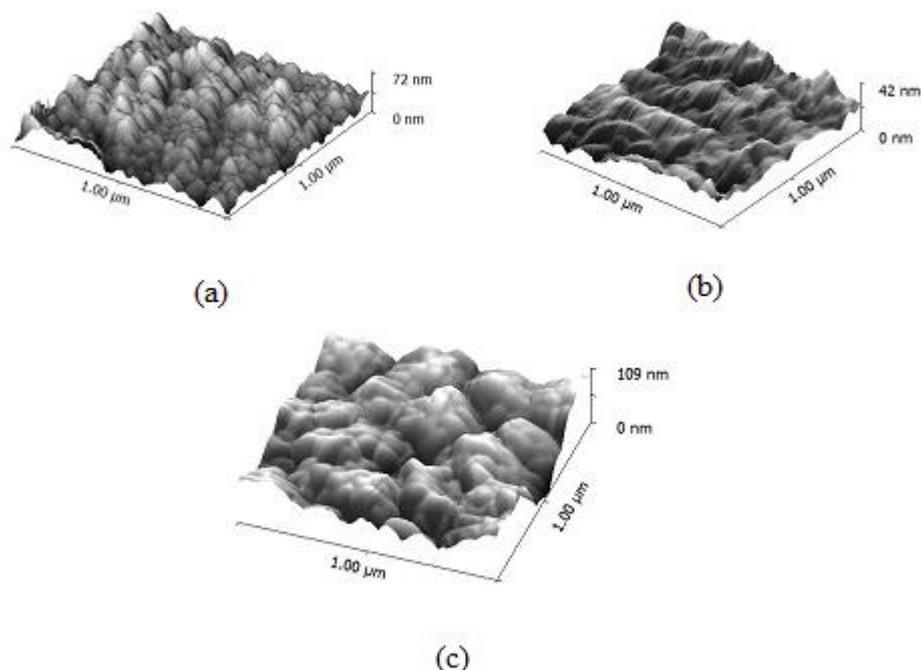


Fig. 6. AFM images of the cadmium sulfide films deposited for 120 min at 333 K from the reaction mixture with the concentrations of the reactants, M: (a) $[\text{CdCl}_2] = 0.02$, $[\text{Na}_3\text{Cit}] = 0.3$, $[\text{CSN}_2\text{H}_4] = 0.4$, (b) $[\text{CdCl}_2] = 0.02$, $[\text{NH}_4\text{OH}] = 2.0$, $[\text{CSN}_2\text{H}_4] = 0.4$, and (c) $[\text{CdCl}_2] = 0.02$, $[\text{Na}_3\text{Cit}] = 0.3$, $[\text{NH}_4\text{OH}] = 2.0$, $[\text{CSN}_2\text{H}_4] = 0.4$ (Scan size $1 \times 1 \mu\text{m}$).

Hydrochemical deposition proceeds in the kinetic region, which makes the temperature a suitable parameter for its effective control [22]. A temperature increase by 20 K under conditions of spontaneous nucleation caused the conversion of the cadmium salt to sulfide to increase from 15 to 70 % (Fig. 2). At the same time, under a controlled solid phase surface area, an increase in the deposition temperature by 15 K only leads to exhaustion of the metal salt in the reaction mixture.

The surface area on the glass powder introduced into the reactor can significantly affect not only the metal sulfide deposition rate but also the morphology and properties of the resulting films [21].

4. Conclusion

This study for the first time summarized the kinetic data on the formation of the solid phase of cadmium sulfide under conditions of spontaneous nucleation and interfacial area control as combined with examination of the kinetics of the formation and evolution of CdS films. This allowed establishing a correlation between the supersaturation level created in the reaction mixture and the growth dynamics and morphology of the layers deposited. These results can provide broader opportunities for controlling the layer microstructure, and functional properties.

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