Nucleation and mechanism of metal sulfide film growth using deposition by thiocarbamide*

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The mechanism of hydrolytic decomposition of thiocarbamide upon the interaction with metal salts with deposition of thin films of sulfide was proposed. The kinetic studies of the transformation of metal salt into sulfide and IR spectroscopy confirmed that one of the hydrolysis products of thiocarbamide was cyanamide. The concept about the activation of thiocarbamide decomposition was extended due to the nucleophilic addition of anions to form an intermediate reaction complex thiocarbamide—metal ion—nucleophile. The activation weakens in the order $OH^- > CH_3COO^- > Cl^- > Br^- > I^-$. The presence and active role of colloidal components of reaction mixtures in the nucleation and formation of films of metal sulfides by chemical bath synthesis were established by spectrophotometric and kinetic measurements. It was concluded that from the viewpoint of fractal formalism metal sulfide films are formed in chemical bath deposition *via* the mechanism of cluster—cluster aggregation in the form of consecutive evolution of structural levels. A complex scheme of the mechanism of chemical bath deposition of metal sulfides by thiocarbamide was proposed. The results of studies of their phase composition, microstructure, and properties are presented.

Key words: thiocarbamide, metal sulfides, thin films, chemical bath synthesis, colloidal phase, fractal dimensionality.

Thin films of lead, zinc, cadmium, and tin sulfides have been demanded for recent decades as functional materials for various fields of technology. They find wide use as detectors of optical radiation,[1,2] photoluminescent materials,[3] thermocouples,[4] solar cells,[5—8] sensors,[9—11] nanostructured catalysts,[12] and quantum dots.[13]

One of the most efficient methods for preparation of metal sulfide films and related solid solutions is hydrochemical deposition (chemical bath deposition, CBD).[1,14—17] However, researchers are primarily interested in studying functional properties of semiconductor materials obtained by this method. Nevertheless, studies considering nucleation processes and the mechanism of subsequent formation of the solid phase of metal sulfides on dielectric substrates, being of primary importance for the microstructure and functional properties of the films, are nearly lacking.

Thiocarbamide (thiocarbonic acid diamide) CH_4N_2S and its derivatives are used most widely as sulfidizers for CBD of metal sulfide layers. However, chemism of the reaction of thiocarbamide with metal salts forming sulfides remains almost unclear. The existing concepts about possible mechanisms of the reaction were considered in detail.[15,18] Generally, the schemes proposed for the deposition of metal sulfide films are based on either the formation of intermediate reaction complexes taking into account high ligand reactivity of thiocarbamide due to the formation of the metal—sulfur coordination bond,[18—20] or its hydrolytic decomposition to form sulfide sulfur.[15] Differences in these approaches are not too important and can supplement each other when studying the whole process. However, although the conditions of nucleation and growth of the metal sulfide solid phase were considered in literature, attention given to the role of colloidal micellar components of solutions seems insufficient, in particular, to colloidal phases of metal hydroxides formed under the conditions of synthesis and to problems of aggregation of primary particles and their structuring in the course of film formation.

The purpose of this work is the study of specific features of the nucleation and mechanism of growth of metal

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sulfide films upon deposition by thiocarbamide taking into account the role of colloidal components of the solution.

Experimental

Objects of the study were chemically deposited thin films of PbS, CdS, SnS, Ag$_2$S, and Cu$_2$S. The hydrochemical synthesis of PbS (CdS) films was carried out from the reaction mixtures containing aqueous solutions of lead acetate (cadmium chloride), sodium citrate, ammonium hydroxide, and thiocarbamide. The reaction mixture including tin(II) chloride, sodium citrate, sodium hydroxide, and thiocarbamide was used for the preparation of SnS film. The Cu$_2$S film was deposited from an aqueous solution containing copper(II) sulfate, ammonium hydroxide, thiocarbamide, and muriatic hydroxylamine that provides the reduction of divalent copper. The Ag$_2$S films were synthesized using silver nitrate and thiocarbamide in an aqueous solution of ammonia.

Films were deposited at 333 to 353 K on the pre-degreased in a chromium mixture glassceramic (CT-150 trade mark) or oxidized silicon substrates 30×24 mm in size in molybdenum glass reactors placed in a LOIP LT-112a thermostat (the accuracy of temperature maintenance was ±0.1 K). The time of synthesis was varied depending on the stated task from 1 to 120 min. The content of soluble forms of lead, cadmium, and tin(II) in the reaction mixtures was determined by back trilonometric titration.[21]

The optical spectra of solutions of lead salts in an alkaline medium were recorded using a Specord UV—Vis spectrophotometer. A JEOL JUS-5900 LV scanning electron microscope was used for electron microscopic studies. The morphology of the surface of metal sulfide films was studied with an Explorer scanning probe microscope (ThermoMicroscopes) in the contact atomic force microscopy (AFM) mode. Silicon nitride (Si$_3$N$_4$) cantilevers with a resonance frequency of 17 kHz were used for scanning of the surface. The elemental analysis of the films in the course of layer-to-layer ion etching was carried out using Auger electron spectroscopy on an ASC-2000 spectrometer (France).

Solutions were centrifuged on an OS-6MTs stationary laboratory centrifuge (Russia) with a rotation frequency of the drive axis of 6000 rpm. The thickness of deposited films was estimated using a MII-4M two-beam interference microscope (Linnik microinterferometer).

Results and Discussion

An analysis of publications concerning the hydrolytic decomposition of thiocarbamide showed more than twenty final products and intermediates of the processes determined experimentally. Among them hydrogen sulfide, cyanamide, urea, guanylurea, guanidine, and ammonium carbonate are met most frequently.[15] However, according to the opinion of the most part of scientists, hydrogen sulfide and cyanamide are still the major decomposition products of thiocarbamide and the process can be reversible. The main argument in favor of the reversibility of the reaction is the demonstrated[22] possibility of thiocarbamide synthesis from hydrogen sulfide and cyanamide.

It should be mentioned that the results of our kinetic studies on the deposition of PbS upon the introduction into the reaction mixture of such potential products of thiocarbamide decomposition as cyanamide H$_2$CN$_2$, urea CH$_4$N$_2$O, guanidine CH$_5$N$_3$, and ammonium carbonate (NH$_4$)$_2$CO$_3$ confirm this point of view. The transformation of lead acetate into lead sulfide is most strongly inhibited by the introduction of cyanamide into the initial reaction mixture. This is indicated by the rate constants of this process (k, min^{-1}) calculated by the first-order equation and taking the corresponding values: 0.022, 0.064, 0.134, and 0.172, respectively.

In addition, according to the data of IR spectroscopy, all deposited metal sulfide films exhibit a characteristic absorption band at $\nu = 1980—2000$ cm^{-1} corresponding to the C=N bonds. We have showed[23] that the content of metal cyanamides in the PbS—CdS films can attain 21 mol.% under certain synthesis conditions.

A comparison of the indices of instability constants (pk_{ins}) for complexes Me(CH$_4$N$_2$S)$_n$ with the indices of solubility products (pSP) of the corresponding sulfides presented in Table 1 clearly demonstrate that the higher the stability of the metal complex, the lower the solubility product of its sulfide. An increase in the pH or temperature sharply increases the tendency of thiocarbamide to decomposition.[15,22] However, according to our calculations, even at pH = 12 the destruction rate in an aqueous solution at 298 K is relatively low and does not exceed $6.4 \cdot 10^{-4}$ mol L^{-1} day^{-1}. This indicates the determining contribution of complex formation to the synthesis of metal sulfides.

The electron density distribution in a thiocarbamide molecule according to published data[18] is presented below.
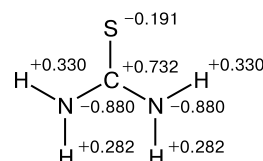
It is seen that a significant positive charge is concentrated on the carbon atom due to the lone electron pair of the sulfur atom and electron density distribution in the

Table 1. Indices of instability constants (pk_{ins}) of the metal complexes with thiocarbamide and solubility products (pSP) of sulfides and the pH of the onset of their deposition (pH$_i$)

| Cation	Complex ion	pk_{ins}[24]	pSP$_{MeS}$[25]	pH$_i$
Hg^{2+}	Hg(CH$_4$N$_2$S)$_4^{2+}$	27.96	52.4	3.0
Ag$^+$	Ag(CH$_4$N$_2$S)$_3^+$	13.14	49.2	3.0
Cu^{2+}	Cu(CH$_4$N$_2$S)$_3^{2+}$	12.82	35.2	5.0
Cd^{2+}	Cd(CH$_4$N$_2$S)$_3^{2+}$	2.92	26.1	6.2
Pb^{2+}	Pb(CH$_4$N$_2$S)$_3^{2+}$	1.77	26.6	6.8
Zn^{2+}	Zn(CH$_4$N$_2$S)$_3^{2+}$	0.73	23.8	13.0

molecule. It was shown using quantum chemical calculations that the nucleophilic addition of the hydroxide ion to the C atom substantially activates thiocarbamide decomposition. The formation of the CH_4N_2S—OH^- complex results in the appearance of an adiabatic charge fluctuation resulting in the selective excitation of the S=C bond on the thiocarbamide molecule. The calculated energy of the sulfur—carbon bond decreases from 10.7 to 8.9 eV, enhancing the reactivity of thiocarbamide with respect to chalcophilic elements due to the facilitation of sulfur elimination.

The concepts on the activation of thiocarbamide from the viewpoint of the nucleophilic addition of the hydroxide ion to the thiocarbonyl carbon atom can be extended by the consideration of the addition of other nucleophiles to CH_4N_2S, in particular, various anions in the reaction mixture. This statement was confirmed by the results of kinetic studies for the deposition of lead sulfide in the presence of anions of different nature. The experimentally determined rate constants of the first-order reaction of thiocarbamide decomposition in the process of PbS formation in the presence of sodium salts NaCH₃COO, NaCl, NaBr, NaI (0.12 mol L⁻¹) at 353 K are given below.

Anion	OH^-	Cl^-	CH_3COO^-	Br^-	NO_3^-	I^-
k/s⁻¹	0.0678	0.0423	0.0404	0.0378	0.037	0.0227

As can be seen, the decrease in the formation constants for PbS correlates with the decrease in the nucleophilicity of anions added to the reaction mixture. The ability of anions to thiocarbamide activation decreases with a decrease in the nucleophilicity from the hydroxide to iodide ion due to a less complete compensation on the charge on the thiocarbonyl carbon atom.

Therefore, the first stage of metal sulfide formation can be the following. At first the nucleophile (Nu) attacks the carbon atom of thiocarbamide, due to which the p-system of the central fragment is violated (*i.e.*, the planar coordination of the molecular structure is distorted) and the sp³-hybridized carbon atom in the tetrahedral coordination formed (Scheme 1).

Scheme 1
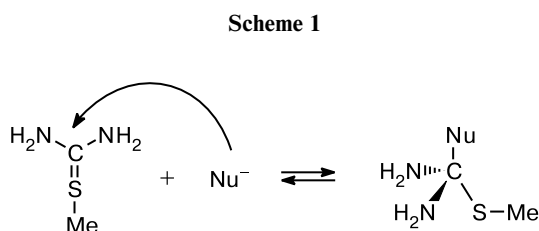
Then the carbon—sulfur bond is cleaved to form cyanamide with the simultaneous elimination of metal sulfide.

The enhancement of the activity of thiocarbamide by nucleophilic addition favors both the hydrolytic decomposition and the formation and subsequent decomposition of its intermediate complex with the metal. However, the

ability of thiocarbamide to dissociation is mainly determined by the degree of weakening of the S=C bond only due to nucleophilic addition, whereas the complex formation mechanism enhances this ability by the simultaneous strengthening of the is M—S bond. From the viewpoint of the final result (metal sulfide deposition), the proposed mechanism is universal and, hence, this mechanism is more probable than the process of "usual" dissociation of thiocarbamide.

A metal sulfide film can be nucleated *via* both the homogeneous and heterogeneous mechanism. This depends on the physicochemical nature of the metal, substrate, and conditions formed in the system. An alkaline medium used for the deposition of metal sulfides by thiocarbamide provides the conditions for the formation of hydroxides in the reaction mixture, including their colloidal forms that actively participate in nucleation.

The diagram of distribution of the ionic forms of lead at 353 K in the $Pb(NO_3)_2$—H_2O—OH^- system calculated from the data on the stability of these forms is shown in Fig. 1. It follows from the diagram that at pH ≈ 11 up to 50% lead in the solution exist in the form of neutral metal hydroxide molecules.

According to the data of spectrophotometric studies of $Pb(CH_3COO)_2$—NaOH solutions, in the working range of pH of lead sulfide decomposition, they contain significant amounts of colloidal forms of metal hydroxide (Fig. 2). An analysis of the spectra shows that with an increase in the alkalinity of the solution the long-wavelength shoulder increases near 44 000 cm⁻¹ due to the formation of complex $PbOH^+$ and a small peak appears at ~39 000 cm⁻¹ caused by the resonance absorption of dissolved $Pb(OH)_2$ molecules. A long-wavelength tail (curves *4—6*) extended to the visible spectral range is observed at pH ≥ 10.7. Its appearance is related to light scattering by colloidal particles of lead hydroxide. After multiple passing the solution
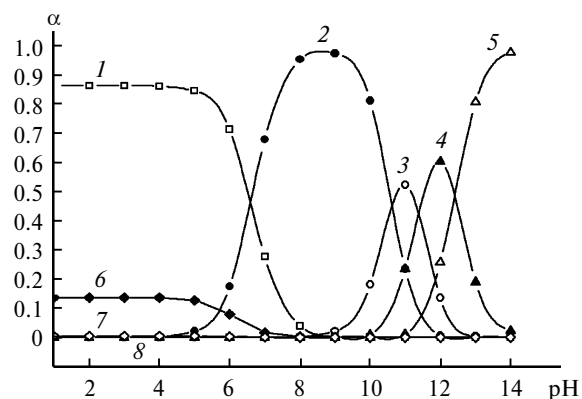
Fig. 1. Distribution diagram of ionic forms of lead in the $Pb(NO_3)_2$—H_2O—OH^- system at 353 K: Pb^{2+} (*1*), $Pb(OH)^+$ (*2*), $Pb(OH)_2$ (*3*), $Pb(OH)_3^-$ (*4*), $Pb(OH)_4^{2-}$ (*5*), $Pb(NO_3)^+$ (*6*), $Pb(NO_3)_2$ (*7*), and $Pb(NO_3)_3^-$ (*8*); α is the fractional concentration of ionic forms of lead.
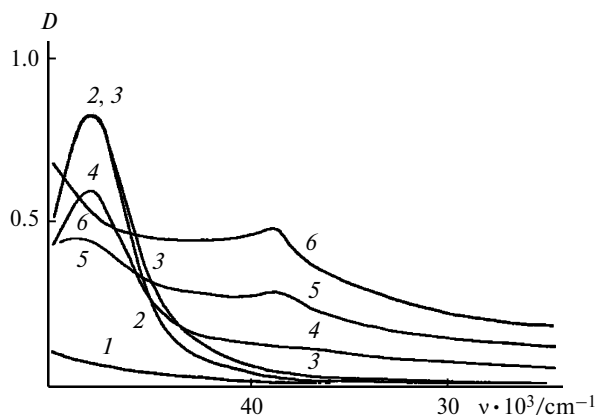
Fig. 2. Optical spectra of solutions in the $Pb(CH_3COO)_2$—NaOH system at the following concentrations of the components, mol L^{-1}: [NaOH] = $1 \cdot 10^{-4}$ (*1*); [$Pb(CH_3COO)_2$] = $1 \cdot 10^{-4}$ (*2*); [NaOH] = $5 \cdot 10^{-5}$, and [$Pb(CH_3COO)_2$] = $1 \cdot 10^{-4}$ (*3*); [NaOH] = $1 \cdot 10^{-4}$ and [$Pb(CH_3COO)_2$] = $1 \cdot 10^{-4}$ (*4*); [NaOH] = $2 \cdot 10^{-4}$ and [$Pb(CH_3COO)_2$] = $1 \cdot 10^{-4}$ (*5*); [NaOH] = $5 \cdot 10^{-4}$ and [$Pb(CH_3COO)_2$] = $1 \cdot 10^{-4}$ (*6*).

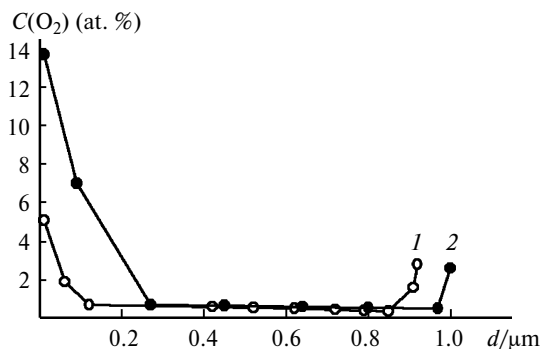**Fig. 3.** Oxygen content ($C(O_2)$) over the thickness of the PbS film obtained from the reaction mixture at the following concentrations of the components, mol L^{-1}: [$Pb(CH_3COO)_2$] = 0.034 (*1*) and 0.067 (*2*); [$Na_3C_6H_5O_7$] = 0.4; [NH_4OH] = 5.0; [CH_4N_2S] = 0.6.

through a microporous filter, which detains colloidal fractions, the long-wavelength scattering band gradually disappears from the spectra.

High-performance centrifuging of solution samples from reactors and the consequent analysis of the fugates showed that the fraction of metal in the composition of colloidal dispersion fractions during sulfide film deposition upon pouring together the reagents ranges within 10—20%.

It is known that the formation of hydroxo colloidal forms of the metal is energetically more favorable at the interface than in the solution bulk. The hydrophilic oxide-containing surface of glass, quartz, or Sitall substrates acts as such an interface. As a result, after pouring the reagents containing the hydrolyzed metal forms, the surface is covered with a mono- or polymolecular hydroxide layer, whose particles act as nucleation sites of the sulfide phase. This phenomenon is especially characteristic of metals forming stable hydroxo complexes (lead, cadmium, tin, zinc, mercury). This process was named in the literature the "hydroxide scheme" of nucleation of metal sulfide films.[26,27]

The considered mechanism confirms the results of elemental analysis by Auger electron spectroscopy of the lead sulfide films deposited from a citrate—ammonia system during their layer-to-layer etching (Fig. 3). A deficiency in the sulfur content relatively to the formula composition PbS is almost always observed over the film thickness and ranges from 0.4 to 14.7 at.%, depending on the deposition conditions. The maximum nonstoichimetry is observed in the layer adjacent to the substrate. The maximum content of oxygen attaining (see Fig. 3) 5.7 or 13.8 at.%, depending on the initial concentration of lead acetate, is also observed. An increase in the oxygen amount in the film composition for the layer >1 μm thick is explained by the

fact that, when a higher initial concentration of lead acetate (0.067 mol L^{-1}) is used, its deposition occurs, which increases the probability of formation of basic metal salts under the conditions of strong oversaturations. The data obtained indicate the presence of oxygen-containing phases in the form of lead hydroxide or basic salts in the near-surface (to the substrate) PbS layers. According to analyses data, the established content of other elements (carbon, nitrogen) does not exceed 2 at.%.

Taking into account considerable differences in the solubility products of metal hydroxide and sulfide, the presence of lone electron pairs at the sulfur and nitrogen atoms in thiocarbamide results in its high adsorption activity toward the hydroxide phase followed by sulfidization. In experimental studies this appears as a significant induction period of sulfide phase formation on the substrate.

It follows from the radiochemical data[15] on the nucleation of the CdS film that when cadmium is present at the substrate from the very beginning of the synthesis, then the content of its sulfide increases sharply in a narrow time range only to the end of the induction period.

The process is also characterized by the shape of the kinetic curves of tin(II) salt transformation into sulfide SnS by the reaction with thiocarbamide (Fig. 4). The wide plateaus in the kinetic curves obtained for different initial concentrations of $SnCl_2$ correspond to the occurrence of sulfidization of the hydroxide phase of tin(II) formed at the initial stage.

The step of hydroxide sulfidization is rate-determining and its rate is determined in fact by the constant content of sulfide sulfur in the system, which is due to the decomposition of thiocarbamide under specified conditions according to the hydrolysis constant.

Thus, colloidal particles of metal hydroxide play the role of an activator of the substrate surface, decreasing the energy barrier for film nucleation, and also serve as nucleation sites of the sulfide phase.
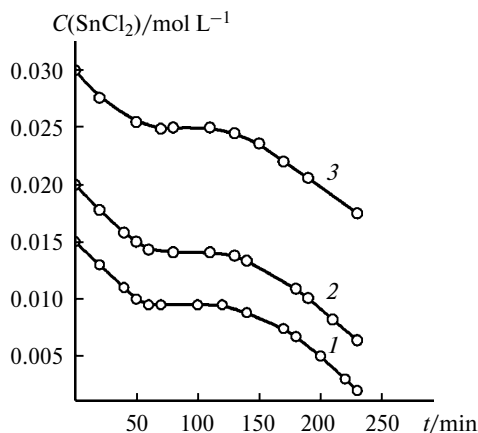
Fig. 4. Kinetic curves of transformation of the tin salt into sulfide at the initial concentration of $SnCl_2$, mol L^{-1}: 0.015 (*1*), 0.02 (*2*), and 0.03 (*3*). The temperature of the process is 353 K. Composition of the reaction mixture, mol L^{-1}: $[Na_3C_6H_5O_7] = 0.3$, $[NaOH] = 0.32$, $[CH_4N_2S] = 0.48$.

The data obtained by studying the kinetics of deposition of metal sulfide films taking into account the results of high-performance centrifuging of the reaction mixtures prove the active participation of the colloidal sulfide-containing fractions formed in the bulk of the reaction mixture in the formation of metal sulfide films. As can be seen from Table 2, the growth rate of the CdS film from an ammonia system even increases in 70 min with a sharp decrease in the content of the ion-soluble forms of cadmium in the reaction mixture. The increase in the thickness of the cadmium sulfide layer can be explained only by the participation of the colloidal micellar components of the solutions in the process.

A similar conclusion was drawn by the authors[28] who considered that the colloidal chemical component of the solution and adsorption phenomena on the substrate surface play the main role in the mechanism of CdS film formation by chemical deposition.

Table 2. Content of ion-soluble forms of cadmium (C(Cd)) in the reaction mixture, relative thickness of the deposited film (h/h_t), and its growth rate (u) at different durations of chemical bath deposition of CdS from an ammonia system

t/min	C(Cd)/C_0(Cd)	h/h_t	u/nm min^{-1}
20	0.86	0.09	1.1
40	0.78	0.18	1.2
60	0.66	0.46	4.2
70	0.55	0.62	4.8
90	0.40	0.78	2.4
120	0.23	0.94	1.6
150	0.10	0.99	0.5
180	0.10	1.00	0.1
200	0.10	1.00	0.0

Traditional molecular kinetic theories of growth are used, as a rule, to explain the growth of metal sulfide films in the hydrochemical synthesis. In these theories, the process of film deposition is considered as a surface effect that occurs in the scales of molecular sizes near the surface. However, the operation with individual atoms and molecules when considering the growth mechanism is justified, in our opinion, only for the initial stages of deposition characterized by weak interactions under the conditions of low oversaturations with respect to the solid phase.

As earlier mentioned validly,[29] crystal growth must be referred to the volume phenomenon rather than to the surface one, *i.e.*, the solution volume actively participates in this process. The principal role in the process belongs to the near-surface layer, which exceeds molecular sizes by several orders of magnitude. The solid phase grows due to molecular aggregates formed in the solution volume. The molecular aggregates are ordered under the action of surface forces at a short distance from the surface and thus gain the quasi-crystalline character. The existence of such molecular complexes, clusters, or aggregates, playing the fundamental role at certain stages of crystal growth, was proved experimentally.[30]

Most likely, it is more correct to present the near-surface zone of the growing film as some transition area, whose structure changes from that characteristic of crystallites to the structure typical of the medium. This structure is formed by molecular aggregates, associates, clusters, submicronic segregations that have colloidal nature or are the products of structuring colloidal particles of metal sulfides and can deposit as individual volume blocks on the surface to form polymolecular layers of growth. Film-forming submicronic aggregates act as unique building blocks. According to published data,[31—33] the size of these blocks at different stages of solid phase formation can range from 5 to 70 nm.

Significant prospects in discovering of the mechanism of new phase formation under the conditions far from thermodynamic equilibrium are provided by the fractal formalism.[34]

Therefore, colloidal micellar particles should be considered as the main primary unit in the hydrochemical synthesis of metal sulfides. The aggregation and reorganization of these particles result in the formation of a branched structure corresponding to principles of fractality: the ability to occupy a large space when using a small amount of the substance, a high sedimentation stability due to the branchy structure and low density, a decrease in the density of colloidal particles to the periphery due to the developed diffuse part, and a low energy barrier for the formation of the ordered structure.

Colloidal particles executing chaotic motions in the volume of the reaction mixture when even a small roughness appears on the substrate surface (for example, due to the adhesion of a single particle) are characterized by a high

probability of aggregation to form a fractal structure. This is associated with the fact that particles moving not only toward the surface but also along the surface or even from the surface can collide with any ledge. Therefore, ledges grow more rapidly and represent active growth sites for the formation of a branched structure having the property of a fractal cluster. From the positions of the fractal cluster approach, the formation of a metal sulfide film from an aqueous solution can be presented as an evolution of consecutive structural forms having the fractal hierarchy. The final structures of the previous level become compacting elements at each next fractal level. The structure, composition, and evolution behavior of fractal clusters with a high free energy determine, to a great extent, the growth mechanism, and the final state and properties of films deposited from aqueous solutions. As this sequence becomes more complicated, critical nuclei (primary particles) and aggregation products of colloidal particles in the form of fractal clusters, aggregates, spheroids, and grains can enter into the sequence.

We calculated the radii of critical nuclei of lead and cadmium sulfides from the comparative kinetic studies for the conditions of spontaneous nucleation and control of the solid phase interphase surface taking into account the values of oversaturation.[35,36] They were 3.1—3.8 and 3.4 nm

for PbS and CdS, respectively, for oversaturations of ~10^3 with respect to the solid phase.

From the viewpoint of the fractal cluster approach, the fractal dimensionality of the surface D is an important tool that characterizes the growth mechanism of the deposited metal sulfide films.[34,37]

The images of the lead and cadmium sulfide films with the pronounced fractal character at the initial stage of their growth and the results of calculation of the fractal dimensionalities of the surface of these layers are shown in Fig. 5.

The calculation results made it possible to establish the value of the desired parameter, which was 1.84 and 1.79 for the PbS and CdS films, respectively. Similar calculations for the Ag_2S and Cu_2S films gave the values of fractal dimensionality equal to 1.83 and 1.79, respectively. The obtained values are < 2 and lie in approximately the same ranges. In terms of the Witten—Sander model, these values correspond to cluster—cluster aggregation (CCA) during Brownian motion,[34] which confirms, as a whole, our assumptions on the aggregative mechanism of growth of chemically deposited films. It is also important that the active growth of the film proceeds *via* the same mechanism (CCA) regardless of the mechanism of film nucleation. A consequence of the considered process are specif-
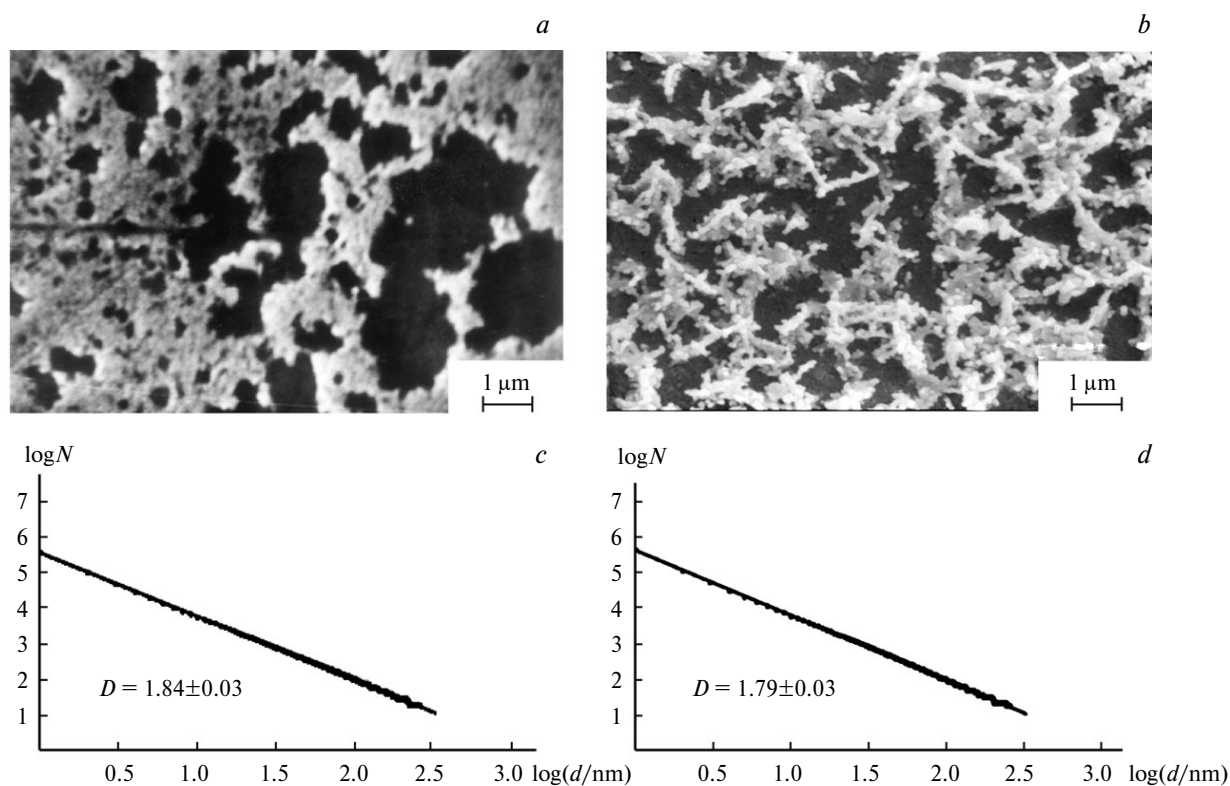

Fig. 5. Images of the PbS (*a*) and CdS films (*b*) in the initial growth step and the results of determination of the fractal dimensionality (*c* and *d*, respectively). Composition of the reaction mixture for PbS films, mol L^{-1}: [Pb(NO$_3$)$_2$] = 1·10^{-2}; [NaOH] = 0.125; [CH$_4$N$_2$S] = 0.057; synthesis temperature 298 K, glassceramic substrate. Composition of the reaction mixture for CdS films, mol L^{-1}: [CdCl$_2$] = 5·10^{-2}; [NH$_4$OH] = 4.0; [CH$_4$N$_2$S] = 0.5; synthesis temperature 353 K, oxidized silicon substrate. Designations are given in text.

ic features of the morphology, microstructure, and properties of deposited polycrystalline metal sulfide films.

According to the results of electron microscopic and optical studies, three to four structural units forming the structural hierarchy can be distinguished in the course of synthesis of cadmium and lead sulfide films. Each of the structures has its time range of formation and development and determines the process rate at a certain stage. Taking into account an increasing ordering of the bonds and internal structure of elements of the sequence and, hence, a decrease in the entropy of the system, one can speak about the self-controlled nature of film formation as a whole. During the growth structural elements of different levels inevitably interact by the contact of the boundary layers. Further these surfaces act as boundaries of crystallites under certain conditions and exert a considerable effect on the mechanical and electrophysical properties of the films.

The evolution of the microstructure in 1 and 3.5 min after the synthesis beginning is well seen on the AFM scans of the PbS films deposited from the citrate—ammonia system (Fig. 6). For average sizes of the aggregates of 200—300 nm, their particles are 30—50 nm in size (see Fig. 6, *b*). Figure 6, *c*, which corresponds to a synthesis time of 5.5 min, microcrystals of halenite with the cubic habitus are already well seen due to the subsequent film ordering.

The sizes of the revealed aggregates for the studied metal sulfides change from 0.01—0.02 to 1.0 μm in the entire structural sequence. One of the indicated structural forms, for example, microcrystallite formation, can be absent or weakly pronounced for a specific metal sulfide.

Based on the above presented results, one can assume the following scheme of the complex mechanism of chemical bath deposition of metal sulfide films by thiocarbamide (Scheme 2). Metal sulfide molecules are formed in the course of the decomposition of the intermediate metal complex with thiocarbamide in the solution bulk and form cluster particles with the fractal structure (**1**). A sublayer of metal hydroxide (**2**) is formed at the substrate when it is placed in an alkaline reaction mixture.

Fractal particles in the bulk participate in the Brownian motion and coagulate to form larger particles (**5**) and adsorb on the substrate upon the collision with the substrate surface (**4**). At the same time, metal sulfide molecules can also be formed on the substrate surface due to the sulfidization of the metal hydroxide layer and adsorbed colloidal particles, resulting in the primary surface particles of the sulfide phase (**3**). As a result of the Brownian motion of particles of the type **1** and **5**, the metal sulfide particles are further aggregated on the surface (**7**). Simultaneously the coagulation of polymolecular particles **5** in

Scheme 2
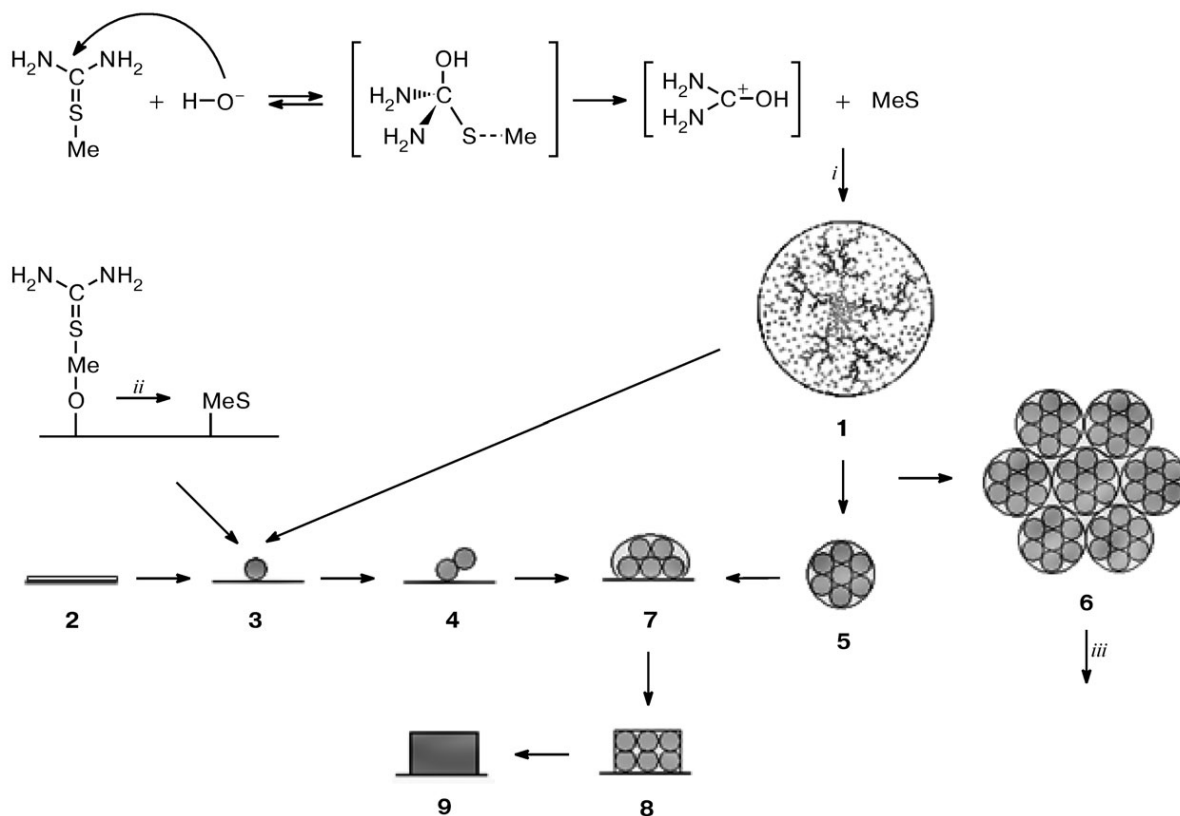
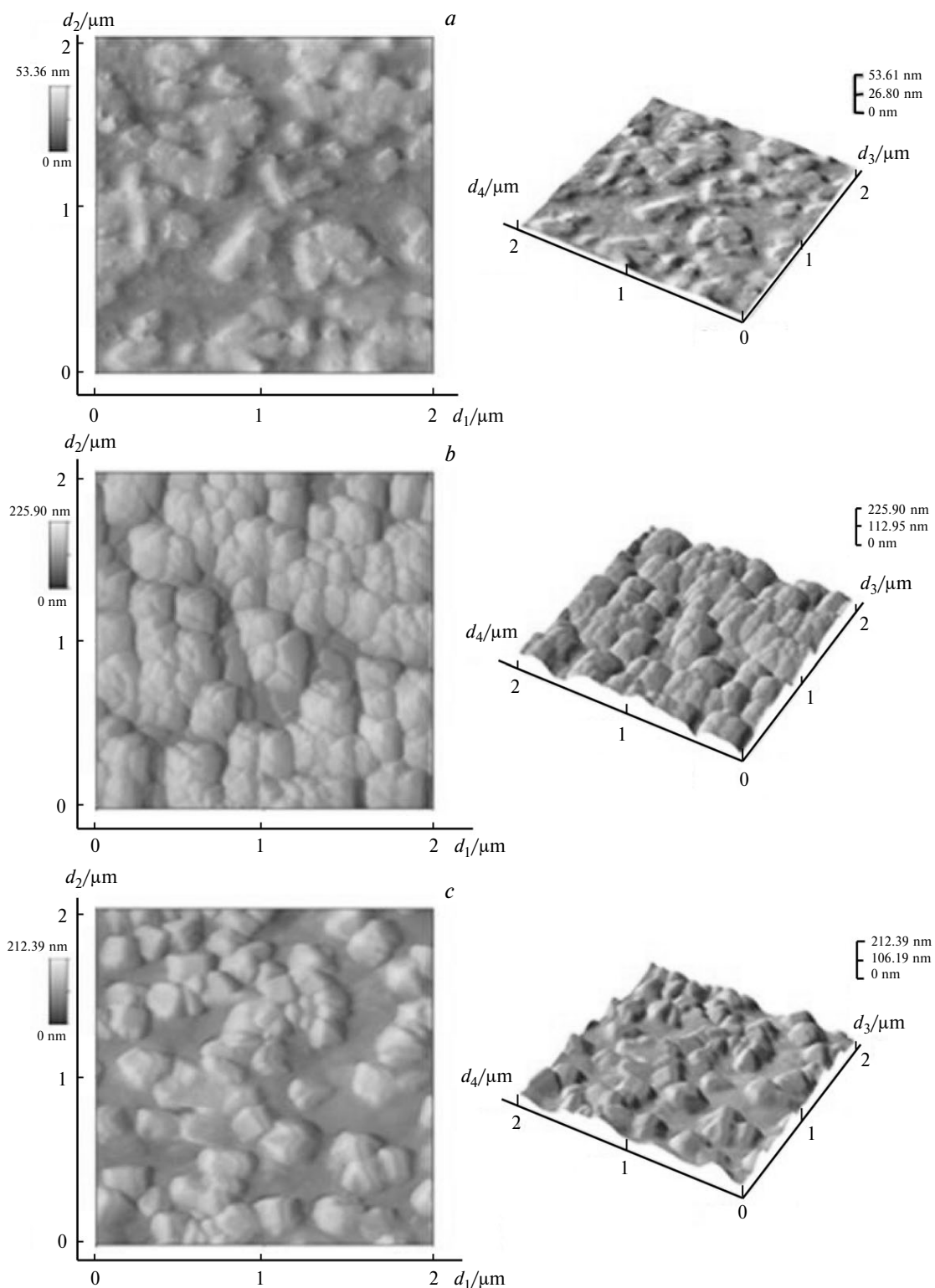*i.* Reaction in bulk; *ii.* Reaction on surface; *iii.* Sedimentation.

Fig. 6. AFM images of the PbS films deposited for 1 (*a*), 3.5 (*b*), and 5.5 min (*c*). Composition of the reaction mixture, mol L^{-1}: [Pb(CH$_3$COO)$_2$] = 0.04; [NH$_4$OH] = 4.0; [Na$_3$C$_6$H$_5$O$_7$] = 0.3; [CH$_4$N$_2$S] = 0.58. Temperature 353 K, glassceramic substrate, scan size 2×2 µm.

the solution bulk leads to rather large aggregates **6** that undergo sedimentation. The particles fixed on the substrate surface (**7**) are gradually crystallized (**8** and **9**).

The principal scheme proposed for metal sulfide film formation upon deposition by thiocarbamide reflects, in our opinion, the key moment of the hydrochemical syn-

thesis and relates all its stages into a single mechanism. It can be assumed that a similar mechanism is also probable for the chemical bath deposition of films of other chalogenide materials.

In a number of our works on the chemical bath deposition of metal sulfide films using thiocarbamide,[38–45] we synthesized and studied the phase composition, crystal structures, morphology, and functional properties of both individual compounds (PbS, CdS, Ag_2S, Cu_2S, ZnS, SnS, In_2S_3) and their substitutional solid solutions ($Cd_xPb_{1-x}S$, $Ag_xPb_{1-x}S_{1-\delta}$, $Cu^I_xPb_{1-x}S_{1-\delta}$, $Zn_xPb_{1-x}S$, $Sn_xPb_{1-x}S$).

The $Cd_xPb_{1-x}S$ ($0 \le x \le 0.15$) films were studied.[38,39] The electron microscopic analysis showed that at the initial deposition period the number of nucleation sites was low and they, as a rule, were related to defects of the substrate surface. Continuous films are formed at a layer thickness of 0.50—0.55 μm. The size of their crystallites ranges from 0.15 to 0.40 μm, depending on the cadmium content. The phase composition of the film was determined by X-ray diffraction analysis, and the changes in the texture and conductivity depending on the synthesis conditions were also evaluated. The films considered were oversaturated substitutional solid solutions with a high level of photoresponse.

The crystal structure, phase composition, and morphology of individual films of lead and silver sulfides and substitutional solid solutions $Ag_xPb_{1-x}S_{1-\delta}$ ($0 \le x \le 0.15$, $\delta = 0.04$—0.08) with sensor properties were studied.[40] The crystal structures and morphology of the synthesized Cu_2S films and substitutional solid solutions $Cu^I_xPb_{1-x}S_{1-\delta}$ ($0 \le x \le 0.086$, $\delta = 0.07$—0.09) were studied by methods of X-ray diffraction, electron microscopy, and Raman spectroscopy.[41] The hydrochemical synthesis of thin films of tin sulfide and solid solutions $Sn_xPb_{1-x}S$ ($0 \le x \le 0.085$) and the influence of components of the reaction mixture on the phase composition and morphology of solid solutions were studied.[42]

The dependence of the structure and morphology of the surface of the synthesized ZnS films and solid solutions $Zn_xPb_{1-x}S$ on their phase composition was established.[43] It is shown that an increase in the zinc concentration results in the complication of the crystal structure, formation of individual grain fragments with sizes from 60 to 100 nm, and changes in the electrophysical characteristics of the layers.

The growth mechanism of the $PbSe_yS_{1-y}$ films was studied by scanning probe microscopy.[44] The results of a comparative analysis of the morphology of layers at the initial stages of growth suggested that the films were assembled by the cluster—cluster aggregation with elements of self-organization.

Thin films of $In_xCu_{1-x}S_yO_{1-y}$ with the indium content up to 9.63 at.% were obtained[45] for the first time by chemical bath deposition from aqueous solutions using thiocarbamide. The distribution and atomic ratios of elements in the synthesized samples were established by X-ray photoelectron spectroscopy. The change in the film microstructure depending on the deposition conditions was revealed by electron microscopy.

Thus, based on the performed kinetic studies, it was proposed to extend the concept on the activation of thiocarbamide decomposition in the reaction mixture with hydroxide ions by the consideration of the addition of other nucleophiles to the carbon atom, whose role can be played by various anions of the reaction mixture. A series of the strength of the nucleophiles was formed by the value of the deposition rate constant of lead sulfide. As a result, it was proposed to interpret the mechanism of metal sulfide formation by the interaction of its salt with thiocarbamide taking into account the formation and subsequent decomposition of the intermediate reaction complex thiocarbamide—metal ion—nucleophile.

The colloidal components of the reaction mixture in the form of metal hydroxide and sulfide play an active role in both solid phase nucleation and subsequent film formation. The use of the fractal formalism for the elucidation of the growth mechanism of metal sulfide films upon their deposition by thiocarbamide showed (according to the results of calculation of fractal dimensionalities) that the process is based on the cluster—cluster aggregation in the form of evolution of structural levels with an increase in their scale structural hierarchy. The principal complex scheme proposed on the basis of the performed studies for the formation and growth of metal sulfide films in the course of chemical bath deposition with thiocarbamide reflects the key moments of these processes and joins all its stages into a single mechanism.

The results of studying the phase composition, structure, morphology, and properties of a series of metal sulfide films deposited using thiocarbamide and related substitutional solid solutions demonstrate wide possibilities of the hydrochemical synthesis of thin film materials with required functional properties.

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