Review

Interaction of metal sulphides in films deposited from solutions of thiourea coordination compounds. Review

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Abstract

Metal sulphides are highly important for the technology of semiconductor film materials. The potential of these compounds has not been exhausted yet when it comes to creating optoelectronic devices, solar cells, and luminescent devices based on them. The goal of this work was to determine the nature of interaction of sulphides in polycrystalline layers of $CdS-Me_mS_n$, where Me are metals of groups I–VII of the periodic table. Cadmium sulphide was chosen as the common component of all studied systems due to the great photoelectric and luminescent properties of this well-studied material.

It was shown that using aerosol spray pyrolysis of the solutions of thiourea complexes, we can obtain solid solutions and chemical compounds of $CdS-Me_mS_n$ at temperatures not exceeding 500 °C. The main electric, optical, and luminescent properties of the layers were described.

It was established that the use of aerosol spray pyrolysis of the solutions of thiourea coordination compounds allows significantly expanding the areas of solubility during the formation of solid sulphide solutions. The specific character of solid-phase interaction and nonequilibrium of the processes occurring during the deposition of layers allow avoiding structural incompatibility of the components expressed in the form of typical factors, such as the non-uniformity of crystal structure, differences in the chemical nature of the components, and discrepancies in sizes of substituting/penetrating atoms.

Under such conditions of deposition of films (the lower threshold of deposition temperatures is determined by the temperature of decomposition of the most thermally stable thiourea coordination compound and does not exceed 250 °C), the solid-phase interactions of most sulphides cannot be achieved. Therefore, the interaction occurs at the moment of thermal destruction of complex compounds due to the emerging valence opportunities of their structural fragments.

Keywords: Metal sulphides, Thiocarbamide coordination compounds, Polycrystalline films, Aerosol spray pyrolysis, Solid-phase interaction

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1. Introduction

In 1962, the first Department of Semiconductor Chemistry in the USSR was opened at the Faculty of Chemistry of Voronezh State University, and in 1965 the "Vysshaya shkola" publishing house published Yakov A. Ugai's textbook for chemistry and physics students of higher educational institutions "Introduction to semiconductor chemistry" [1]. In 1965, Yakov Ugai defended his doctoral dissertation in chemistry on the topic "A study in the field of semiconductor phases based on antimony, arsenic, and phosphorus". Apart from $A^{III}B^V$ compounds that are by their nature coordinate compounds in a solid state, he also studied such semiconductors as $A^{II}B^{IV}$, $A^{II}B^{VI}$, $A^{I}B^{V}$, and others. For his series of works on chemical semiconductor thermodynamics, in 1981 Y. A. Ugai was granted an honorary title of the USSR National Prize laureate in the field of science, the first such title in the history of VSU.

Yakov Ugai was the founder and long-standing head of the scientific school of chemical study of semiconductors. At first, all studies were conducted on massive crystals, but the needs of modern microelectronics required the miniaturisation of devices, so the interest to thin-film technologies increased. VSU's Department of General and Inorganic Chemistry started working on synthesis and study of the properties of semiconductor films. Among the promising methods of deposition of wide-band semiconductor films was aerosol spray pyrolysis (ASP, originally named the method of "solution spray"). Evgeny M. Averbakh, Viktor N. Semenov, and Oleg B. Yatsenko, employees of the department, began working on the application of this method for the deposition of metal sulphides. Over the past years, we have continued exploring this topic in line with the scientific field developed by Y. A. Ugai in 1960s.

Metal sulphides with promising optical, electrical, and luminescent properties are indeed highly important for the film technology of semiconductor materials. A number of devices were created based on them, such as radiation receivers and converters, thermal resistors, etc. At the same time, the potential of these materials has not been exhausted yet when it comes to creating optoelectronic devices, solar cells, and luminescent devices based on them.

In this regard, there is a promising chemical method of obtaining the films of metal sulphides based on thermal destruction of *thiourea coordination compounds* (TCC). Thermal destruction was conducted by spraying aqueous solutions of coordination compounds on a heated substrate, which is the technological basis of aerosol spray pyrolysis [2]. The conditions for the growth of polycrystalline layers of metal sulphides were created. This method can be used for the deposition of metal sulphides of groups III(*a*)–V(*a*) (Ga, In, Sn, Pb, Bi), transition metals I(*b*)–II(*b*) (Cu, Ag, Cd, Zn), and groups VI(*b*)–VIII(*b*) (Cr, Mn, Fe) of the periodic system (Table. 1).

The method offers great possibilities for the formation of thin-film compositions both on dielectric (quartz, sitall) and transparent conductor (doped SnO_2) substrates. Thus, using only a "spray" technology, we obtained heterostructures $SnO_2/Cd_xZn_{1-x}S/Cu_{2-x}S$ that are able to work as photoelectric converters [3]. Recently, it has been found that using thiourea as a sulphidising reagent without changing the deposition method, some sulphides (In_3S_4, $CuInS_2$) can be obtained not only on glass-shaped but also on single-crystal substrates, including silicon, gallium arsenide, indium phosphide, and other $A^{III}B^V$ [4–6]. Such films have a number of specific features, the principal of which is their expressed orientation in relation to the substrate.

From the point of view of chemistry of sulphides and applied tasks of inorganic material science, it is important that using ASP, we can obtain layers of sulphides of different metals with random bulk composition. Also, depending on the nature of sulphides and conditions of deposition, the interaction of the components in the layers varies from the formation of a simple heterophasic mixture to limited solid solutions and chemical compounds of sulphides. It is notable that the release of such compounds and solid solutions on a substrate occurs at relatively low temperatures. Aerosol of TCCs dissolved in water decomposes in the range of temperatures 250–500 °C, however, in order to dope, for example, cadmium sulphide with activators (Cu, Mn, etc.), it is sufficient to introduce the corresponding addition of Cu^{2+} and Mn^{2+} salts to the TCC solution [$Cd(thio)_2Cl_2$]. The study of solid-phase interactions of sulphides in films deposited using ASP has become a separate

Table 1. Physical properties of metal sulphides deposited from solutions of thiourea coordination compounds using ASP

	Sulphide	E_g, eV	E_{pc}, eV	E_{pl}, eV	σ, cm/m	ρ, g/cm³
I	$Cu_{1.76}S$	1.8	–	–	$8 \cdot 10^4$	–
	Ag_2S	1.2	–	–	$6 \cdot 10^{-1}$	–
II	**CdS**	**2.4**	**2.3–2.6 ***	**1.48** **1.58** **1.70**	**$(0.2–11.2) \times 10^{-7}$ ***	**4.82**
	ZnS	3.60	3.5	2.65	$8 \cdot 10^{-7}$	4.25
III	Ga_2S_3	2.85	3.11	1.80	$3 \cdot 10^{-8}$	3.45
	In_2S_3	2.3	2.3	1.66 2.3 2.8	$1 \cdot 10^{-3}$	4.60
IV	SnS	1.2	–	–	$1 \cdot 10^{-2}$	–
	SnS_2	2.2	2.3	–	$1 \cdot 10^{-5}$	4.80
	PbS	0.4	0.8 1.1	–	$1 \cdot 10^{-1}$	7.45
V	Bi_2S_3	1.4	1.46	–	$1 \cdot 10^{-3}$	7.10
VI	Cr_2S_3	1.1	–	–	$4 \cdot 10^{-2}$	–
VII	MnS	2.5	–	–	$5 \cdot 10^{-6}$	–
VIII	FeS_2	1.3	–	–	$6 \cdot 10^{-3}$	–

Designations: E_g is band gap; E_{pc} is photoconductivity band; E_{pl} is photoluminescence band; σ is specific electric conductivity; ρ is density.

* Depending on the initial TCC

task. It includes: *a)* determining the mechanisms of deposition of "mixed" layers and formation of phases with different chemical nature in them and *b)* the dependences of properties of "mixed" layers on the composition and nature of solid-phase interactions.

In this work we discuss the properties of films of sulphide systems with the participation of cadmium sulphide. The goal of the work was to determine the nature of interaction of sulphides in the CdS–Me$_m$S$_n$ layers. Cadmium sulphide was chosen as the common component of all the studied systems due to its great photoelectric and luminescent properties of this well-studied material.

## 2. Formation of metal sulphides from thiourea coordination compounds

The idea of aerosol spray pyrolysis is simple and involves the following. We chose the cation-forming salts that are soluble in some solvent (usually it is water, more rarely ethanol or mixtures of ethanol and water) and reagents that are required for the delivery of the anion former. The obtained solution was sprayed on a heated substrate where after the evaporation of the solvent (or with the participation of the solvent) the components decomposed, leaving a layer of the most thermally stable substance forming a film on the substrate. Thiourea (thiocarbamide, $SC(NH_2)_2$) is a promising sulphidising agent used to obtain the films of metal sulphides. This is due to a number of reasons, among which are low temperatures of the start of aerosol decomposition (from 200 to 300 °C) and high coordination affinity of thiourea to cations of various metals [7]. It was reliably established that the deposition of sulphide films in the studied method occurred through the stage of formation of a coordination compound of thiocarbamide with a metal salt.

TCCs of metals are various in their composition and structure, thermal stability, and mechanisms of thermal destruction. It should be noted that we only refer to true coordination compounds (CC) with the participation of thiourea which is able to produce ionic complexes and inclusion compounds with a number of *s*- and *p*-elements [7]. Apparently, these compounds did not result in the formation of the corresponding sulphides due to the ion-dipole nature of chemical bonds

as compared to true TCCs. In the latter ones, thiourea is always coordinated through an atom of sulphur of thiocarbamide group (S=C) and can act both as terminal and bridge ligands (in such compounds as [Cu(thio)$_2$Cl], [Bi(thio)$_3$Cl$_3$], etc.) [7, 8]. The existence of covalent bonds of Me–S determines the mechanism of sulphide formation by direct introduction of sulphur atoms into the composition of the immediate environment of the metal atom. This explains the great difference of the method of obtaining sulphides from TCCs from hydrolytic methods.

In the complexes with coordination number of 4, such as cadmium, copper, and zinc complexes, the central atom was in the state of sp^3- hybridisation, so the configuration of its immediate environment can be considered to be a distorted tetrahedral one. The configuration of the immediate environment meant the position of atoms that were directly related to the complexing agents by covalent bonds. It should be noted that molecules or ions of thiocarbamide coordination compounds have low symmetry. For instance, particle [Cd(thio)$_2$Cl$_2$] had a symmetry of either point group C_2 (in this case it was chiral), or point group C_S [8, 10–11]. At the same time, the symmetry of the immediate environment was increased and could be described by point groups C_{2v} – in such structures as [Cd(thio)$_2$Hal$_2$] (here Hal – is halogen); C_{3v} – in such structures as [Cu(thio)$_3$Cl]; T_d – in such structures as [Cd(thio)$_4$]$^{2+}$. Analysis of the composition and structure of the coordination compounds that acted as the starting material for the formation of the sulphide phase, allowed drawing a fundamental conclusion that fragments of the sulphide structure started forming in the inner sphere. In case of S→Me coordination with the use of p_y AO S, the order of the C–S bond may decrease (Scheme (1), Fragment I). It is well-known [7] that S-coordination of thiourea causes a shift in the frequencies of valence bonds ν_{CS} into the long-wave region, while frequencies ν_{CN} and δ_{NCN}, by contrast, shift to the short-wave region of the IR spectrum. Thus, the decrease of the order and weakening of the C–S bond with simultaneous reinforcement of the C–N bonds in the TCCs created conditions for the elimination of the organic residue in case of thermal excitation (Scheme (1), Fragment II).

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\tag{1}
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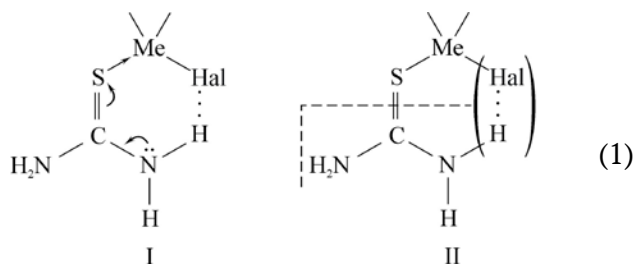
The immediate environment of the complexing agent influenced the formation of various point defects in the metal sulphide lattice. As we know, there is always a variability of complex forms in the solutions of metal salt, and their distribution depends on the composition (gross composition) of the solution. Previous experimental and theoretical studies [12–13] provide a better understanding of this distribution in case of different cadmium salts. Depending on the nature of the salt and composition of the solution, different coordination forms may dominate, and in addition to molecules of thiocarbamide the inner sphere may include anions of Cl$^-$, Br$^-$, I$^-$, CH$_3$COO$^-$, and, under certain circumstances, SO$_4^{2-}$. Therefore, the immediate environment of a cadmium atom may include atoms of sulphur, halogens, and oxygen, and in case of thermal destruction some of the Cd–Hal or Cd–O bonds remain, and defects Hal$_S^+$ and O$_S$ are formed in the sulphide lattice [14–15]. The use of coordination compounds with an inner coordination sphere saturated with thiocarbamide, such as [Cd(thio)$_4$]F$_2$, allowed obtaining sulphides with the composition that is very close to stoichiometric, and the introduction of additives of selenium-(SeC(NH$_2$)$_2$) and tellurium carbamide (TeC(NH$_2$)$_2$) allowed doping metal sulphides with selenides and tellurides.

The influence of the composition and structure of starting coordination compounds on the crystal structure of deposited sulphides is of great interest. Thus, depending on the covalent radius of halide ligands in the [Cd(thio)$_2$Cl$_2$], [Cd(thio)$_2$Br$_2$], [Cd(thio)$_2$I$_2$] series, the structure of the deposited cadmium sulphide changed from wurtzite to sphalerite. In case of a complex compound [Cd(thio)$_2$(ac)$_2$] (ac is ion acetate), the wurtzite modification of cadmium sulphide was deposited together with the sphalerite one, while in case of the compounds with the inner coordination sphere saturated with thiocarbamide [Cd(thio)$_4$](NO$_3$)$_2$ and [Cd(thio)$_4$]SO$_4$, a sulphide of mostly sphalerite

modification was formed [11, 14]. Thus, point symmetry and the composition of the inner sphere of thiocarbamide complexes influenced the spatial symmetry and defect structure of metal sulphides, which allowed purposefully influencing a number of properties of films.

Another important aspect of the influence of the processes of formation of complexes on the properties of sulphide films is a possibility to control the state of oxidation of the cation-forming metal with a variable oxidation state. In this context, a typical example is copper sulphide (I) obtained from thiocarbamide coordination compounds of copper.

The formation of complexes of copper chloride (II) with thiocarbamide is associated with redox processes, as a result of which copper (II) is reduced to copper (I) [7, 16]. The process is preceded by the coordination of a thiocarbamide molecule, and such mutual influence of ligands leads to a homolytic break in the Cu–Cl bond in the inner sphere of the complex [17–18]:

$$(NH_2)_2C=S-Cu\leftarrow Cl \quad \rightarrow \quad (NH_2)_2C=S-Cu^. + Cl^.$$
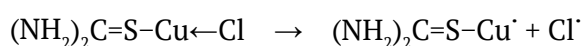
(the scheme shows a part of the coordination environment of the copper ion). In [17] it is assumed that the separated radicals of Cl· oxidise water, and the overall scheme of the process is as follows:

$$4CuCl_2 + 4SC(NH_2)_2 + 2H_2O \rightarrow$$
$$\rightarrow 4[Cu(SC(NH_2)_2)]Cl + 4HCl + O_2.$$
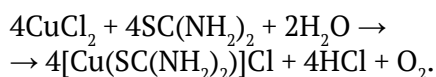
The displacement of chlorine anions into the inner sphere was achieved by the increase in the ratio of concentrations of C_{thio}/C_{CuCl_2}, which allowed increasing to some extent the portion of copper (II) in the solution. The processes similar to those described above also occurred in case of ferrous chloride (III), where, as we proved experimentally, the oxidation state of Fe^{2+} was stabilised in the presence of thiocarbamide. Thus, by varying the concentration of metal salt and thiocarbamide in the solution, we can regulate the oxidation state of the cation-forming metal.

It should be noted that if doping sulphides with anion formers, substitutes in the anion sublattice were achieved by the introduction of the complexes of corresponding ligands to the inner sphere, then doping with cation formers can be achieved by the introduction of the additives of salts of corresponding metals to the initial solution. As a rule, in this case, a substitutional solid solution is formed at first, and then an interstitial solid solution is formed [19]. Thus, we obtained the luminescent layers of CdS and ZnS, activated by Cu^{2+} and Mn^{2+} ions, as well as Cl^- and Br^- [19–21].

Therefore, unique conditions for predicting the properties of sulphides and controlling them were created during the synthesis of metal sulphides from thiocarbamide coordination compounds.

The processes occurring when the aerosol solution reaches the heated substrate are complex and are characterised by significant nonequilibrium. The behaviour of the solvent in a dispersed, quickly heated medium of aerosol has not been thoroughly studied. According to our studies, a series of approximations can be used that suggest either instant evaporation of the solvent similar to quenching, or gradual evaporation that leads to the concentration of the solution, the change in the distribution of coordination forms, and, finally, to the release of crystals of the complexes that are subject to thermal destruction.

Thermal destruction of thiocarbamide complexes is thought to occur due to the thermal excitation of the C–S bond in the coordinated molecule of thiocarbamide [9]. At the same time, there is an opinion that the excitation of this bond was caused by negative charge fluctuation that was localised on the complex upon the destruction of hydrogen bonds in the crystal of coordination compound when it was melted [22]. However, despite the differences in the opinions on the nature of elementary act of thermal destruction, we can formulate the principal concepts characterising this process.

As it was noted before, in the IR spectra of all thiocarbamide complexes we observed a shift in the stretching vibration bonds of the C–S and C–N bonds to the long-wave and short-wave regions respectively, as compared to the position of the bands of the uncoordinated molecule of thiocarbamide. Such changes in the spectrum were due to the redistribution of the electron density in the $SC(NH_2)_2$ molecule that was related to the metal ion through the sulphur atom. The order of the C–S bond in a "free" molecule of thiocarbamide was 1.5, but in case of coordination to the metal ion it decreased to around 1. The order of the

C–N bond, on the contrary, increased due to the involvement of non-separated electron pairs of nitrogen atoms in π-conjugation. Analysis of the IR spectroscopic data allowed stating that as a result of thermal influence on a thiocarbamide complex, such redistribution of the electron density became even deeper, which led to the destruction of the complex due to the disassociation of the C–S bond (Scheme (1)). This scheme showed only the main features of the process and did not provide a full description of pyrolysis, complicated by a series of transformations of the organic residue [23].

The pyrolitic break-down of the C–S bonds may be preceded by the stages of isomerisation of complexes and transformations both occurring in the inner sphere and related to the appearance of ligands in the inner sphere. The transformations in the inner sphere may be associated with the changes in the denticity of ligands (for example, a decrease in the denticity of ligand SO_4^{2-} in the $[Cd(thio)_2 bi\text{-}SO_4]$ complex), while the appearance of ligands in the inner sphere can be considered as the formation of intermediates with the lowered coordination number. For instance, during the thermal destruction of the $[Cd(thio)_2 I_2]$ compound we discovered an intermediate compound $[Cd(thio)I_2]$ formed as a result of elimination and appearance of one molecule of thiocarbamide in the inner sphere [24]:

$$[Cd(thio)_2 I_2] \rightarrow [Cd(thio)I_2] + thio.$$

This can be explained by the mutual influence of the ligands, in particular, by steric difficulties caused by the significant covalent radius of iodine atoms located in the neighbouring vertices of the distorted tetrahedron.

The conducted studies allowed determining the following main features of the synthesis of metal sulphides using TCCs (quoted in [2]).

1. The influence of the TCC structure on the structural defect of the sulphide, including both its impurity and internal disorder caused by the existence of a genetic bond between the immediate environment of the complexing agent in the TCC and the first coordination sphere of the cation former in the sulphide lattice.

2. The dependence of the crystal-chemical structure of sulphide phase allowing polymorphism or forming several stoichiometrically similar independent phases on the symmetry of TCC.

3. The possibility to control the oxidation state of metal in a solution and, therefore, the content of the corresponding phase in a film based on the change in the structure of thiourea coordination compounds by replacement or intentional choice of acidoligands.

3. CdS – $Cu_{2-x}S$ and CdS – Ag_2S systems

The CdS–$Cu_{2-x}S$ system is of interest due to the fact that cadmium sulphide is an electronic semiconductor, while copper sulphides are hole semiconductors, and electrical conductivity of polycrystalline CdS and $Cu_{2-x}S$ may differ by ~ 10^6 times. Such conditions result in some interesting electrical effects observed in thin polycrystalline layers that contain semiconductor phases with different electrophysical properties.

Under the conditions allowing joint deposition of cadmium and copper sulphides as macrohomogeneous layers (T ≈ 350 °C), the phase of the $Cu_{1.76}S$ digenite is deposited that contains four-coordinated atoms of copper in tetrahedral voids of the thickest packings of S atoms [25].

According to X-ray phase analysis, the interaction in mixed layers containing CdS and $Cu_{1.76}S$ is reduced to the limited solubility which does not exceed 5 mol% both on the part of cadmium sulphide or copper sulphide. However, as the results of electrophysical measurements show, such an interaction is of more complex nature. The non-monotonic dependence of electrical conductivity of films on the composition with a minimum in the region of 5 mol% $Cu_{1.76}S$ (fig. 1) indicated the presence of limited solubility on the part of CdS, although the extrema position should not be directly linked to the position of the border of the region of solid solutions. According to photoluminescent data [19], substitutional solid solutions CdS(Cu) were formed with the concentration of copper up to 0.1 at%, and the appearance of acceptor centres Cu_{Cd}^- should result in the compensation of the n-conductivity of CdS. When doping cadmium sulphide with copper additives greater than 0.1 at%, Cu atoms started penetrating into interstitial sites, thus forming Cu_i^+ donor centres. Being relatively small donors [27], these centres were ionised at normal temperatures:

$$Cu_i \rightarrow Cu_i^+ + e^-,$$

creating a reverse effect. Based on the suggestion about the change of mechanism of solubility of small

lg σ (σ / S/m)
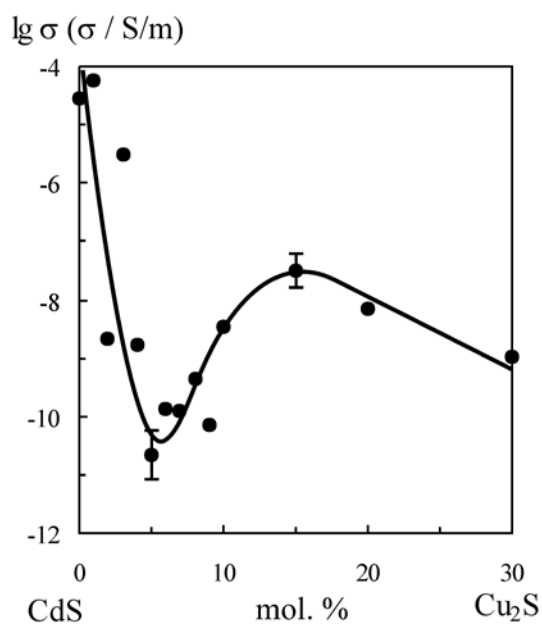
Fig. 1. Dependence of specific electric conductivity of CdS–Cu$_{1.76}$S films on the composition on the part of CdS

amounts of copper in CdS, the minimum of electrical conductivity near bulk composition of 5 mol% Cu$_{1.76}$S can be explained by the release of substitutional solid solutions and further penetration when crossing the concentration bulk threshold of 5 mol%. With such concentration the second phase (*p*-Cu$_{1.76}$S) was almost compensated, and film properties were determined by the main phase of *n*-CdS.

The described mechanism of behaviour of impurities is apparently typical for other sulphides that are poorly soluble in cadmium sulphide and do not form chemical bonds with it. Based on the data of X-ray phase analysis, in the films of the CdS–Ag$_2$S system we found solid solutions with the region of existence < 1 mol% on the part of CdS and ~ 5 mol% on the part of Ag$_2$S. At the same time, the minima of electrical conductivity accompanying the formation of solid solutions were noticeably shifted in relation to those borders that were determined by X-ray phase analysis. Extreme behaviour of electrical conductivity near 50-60 mol% Ag2S was specific for heterophase films and could be related to an increase in the dissipation of carriers at grain boundaries. In such cases, the extrema on "composition – property" diagrams should not be associated with the chemical interaction of the components in the thin layer. From the point of view of current carrier behaviour, a polycrystalline film is a system

of randomly placed potential pits and barriers, which is markedly expressed in case of mixed films. Multiple experimental data showed that the effects related to the appearance of such nonperiodic potential became noticeable near equimolar (bulk) compositions when the microstructure of a film was most imperfect.
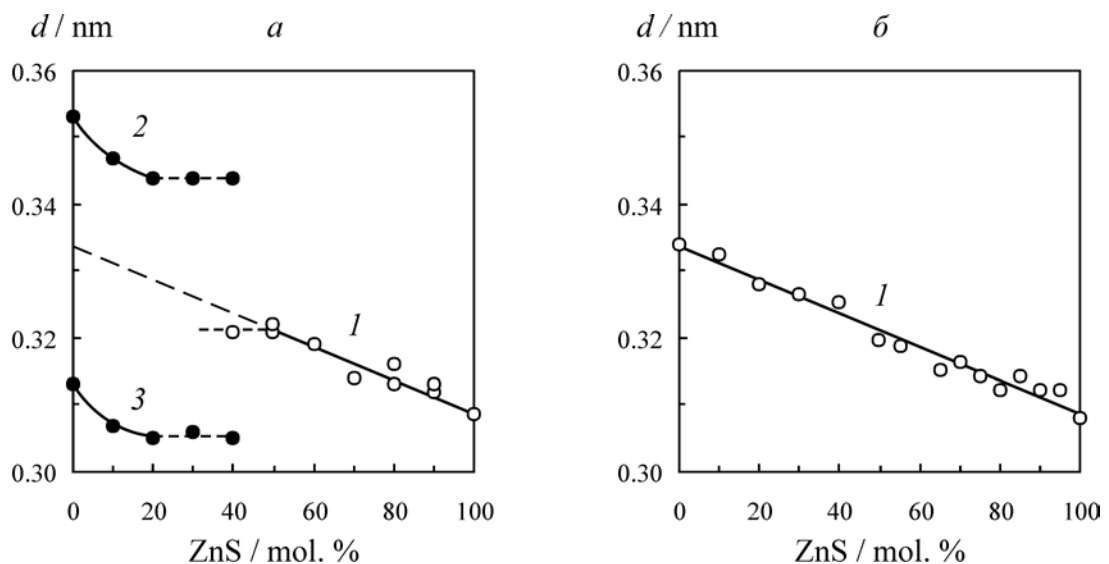
4. CdS–ZnS system

This system is one of the most important on the practical level, thus it attracts the close attention of researchers [28–30]. When studying the specific features of the interaction in this system, it should be taken into account that in case of using TCCs [Zn(thio)$_2$Cl$_2$] and [Cd(thio)$_2$Cl$_2$], zinc sulphide is deposited in a sphalerite modification, while cadmium sulphide is deposited in a modification with the wurtzite lattice [2, 11]. Due to this circumstance, the continuous solubility between hexagonal CdS and cubic ZnS was eliminated. Indeed, the analysis of concentration dependences of properties (Fig. 2) showed typical features of the change of nature of dependence with the compositions of about 18 and 80 mol% ZnS. Therefore, three "composition – property" sections were found on the curves, which indicated the formation of limited solid solutions based on hexagonal CdS on the one hand and cubic ZnS on the other hand. The limited solubility was confirmed by the data of X-ray phase analysis (Fig. 3a), according to which the structure changed from wurtzite (CdS) to sphalerite (ZnS) when the total amount of zinc sulphide in a film increased.

At the same time, photoluminescence spectra of CdS–ZnS films showed a continuous shift of the band within the range of 1.4–2.4 eV accompanied by a non-monotonic change in its intensity. Maximum radiation intensity was observed for the equimolar composition 50 mol%. Apart from the "main" band shifting according to Fig. 2a, there were also radiation bands 520 and 830 nm. They were related to the presence of oxygen in sulphides ZnS and CdS and were not shifted when the composition was changed. The introduction of oxygen during the process of deposition of layers was related not only to the common influence of an oxidising atmosphere where the layer grew, but also to the need to compensate for structural distortions [31]. This, in its turn, led to the inclusion of a greater amount of oxygen for the films approaching an equimolar composition. It is notable that the
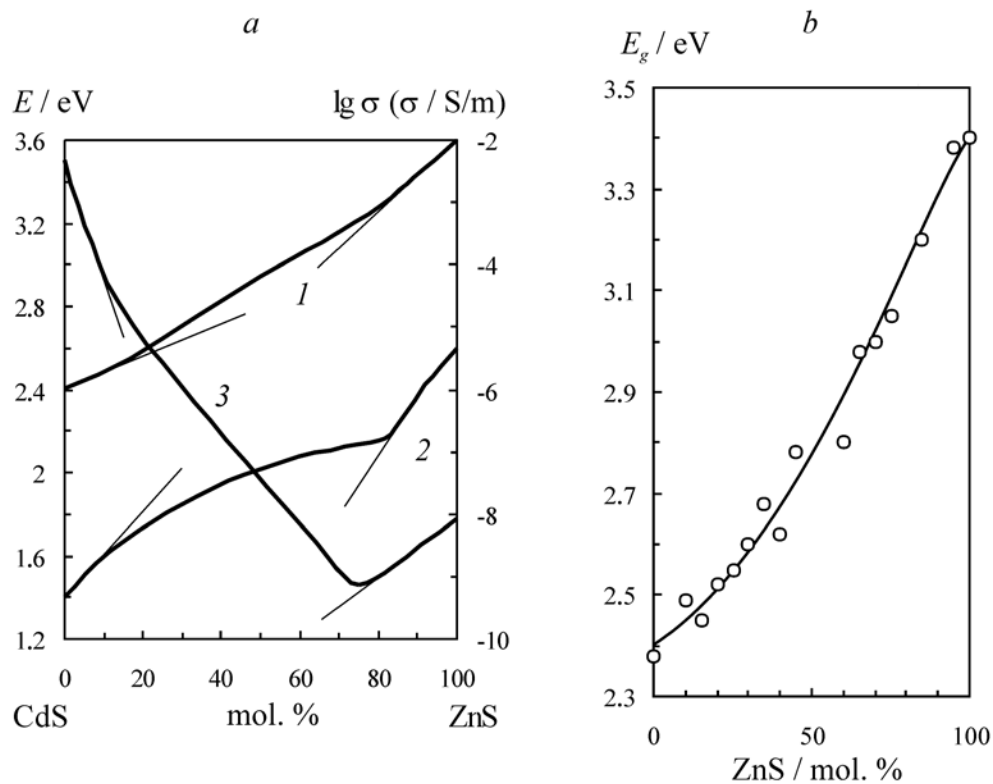
Fig. 2. Concentration dependences of the optical band gap (*1*), spectral position of the luminescence maximum (*2*), and specific electrical conductivity (*3*) of the CdS–ZnS films deposited from chloride (*a*) and acetate (*b*) coordination compounds

Fig. 3. Concentration dependences of the interplanar distances for the solid solutions of the CdS–ZnS system deposited from chloride (*a*) and acetate (*b*) coordination compounds *1*) reflection 111 for a cubic solid solution; *2*) reflection 100 for a hexagonal solid solution; *3*) reflection 101 for a hexagonal solid solution [11]

layers obtained at high temperatures (500 °C) and containing more than 50–60 % ZnS turned out to be X-ray amorphous. We can assume that the inclusions of the ZnO phase under the conditions of oxygenation of a film contributed to the amorphisation. The spectral position of the band of intrinsic conductivity changed only according to the change in the band gap.

It was possible to deposit a series of CdS–ZnS solid solutions in the form of films when using coordination compounds, the thermal destruction of which resulted in the release of a cubic sphalerite modification of cadmium sulphide. An acetate complex $[Cd(thio)_2(ac)_2]$ can be used for that purpose [11]. As Fig. 2b shows, the nature of the dependence of the band gap on the composition changed: the dependence became smooth, without typical sharp curves which would be indicative of reaching the boundaries of the homogeneity region and the decomposition of a solid solution. Interplanar distance d_{111} for these films changed continuously and linearly together with the composition according to Vegard's law (Fig. 3b). An example of the CdS–ZnS system is important as it showed the influence of coordination precursors not only on semiconductor properties but also on polymorphic modifications of sulphides that can exist in several crystalline forms. This way various phase states and different solid-phase solubility in the deposited layers were realised.
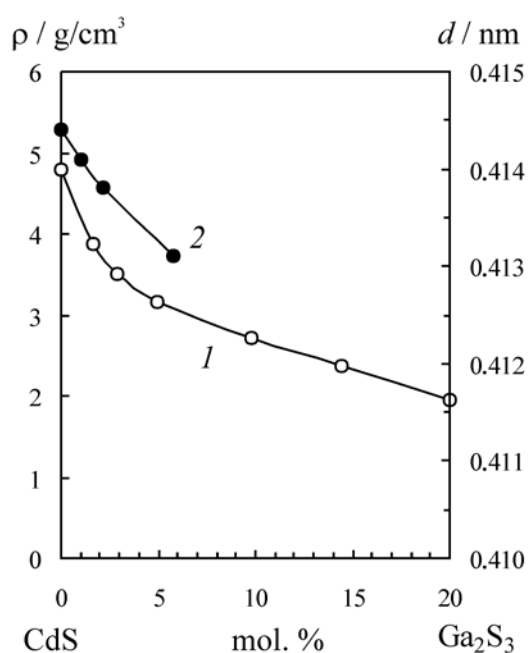
## 5. CdS – Ga$_2$S$_3$ system

The solubility of cadmium sulphide in Ga_2S_3, discovered from the data on concentration dependences of the optical band gap, electric conductivity σ, and pycnometric density ρ was evaluated as ~ 5 mol% CdS. The most reliable data on the range of the area of existence of solid solutions on the part of CdS were obtained from the concentration dependence of density and interplanar distance d (Fig. 4). The nature of changes in these parameters near pure CdS indicates the limited solubility within 5 mol% Ga_2S_3. The existence of the $CdGa_2S_4$ compound described in previous studies in the films of the CdS–Ga_2S_3 system cannot be conclusively established despite the satisfactory coincidence of some characteristics of the films of equimolar composition with the characteristics of this compound.

6. CdS – In$_2$S$_3$ system

A chemical compound with a spinel structure, $CdIn_2S_4$, was found in this system [32]. The extrema appearing at 50 mol% In_2S_3 on concentration dependences of the band gap and pycnometric density of CdS–In_2S_3 films also confirmed the existence of this compound (Fig. 5). The main

Fig. 4. Density (*1*) and lattice parameter (*2*) of the CdS–Ga$_2$S$_3$ films
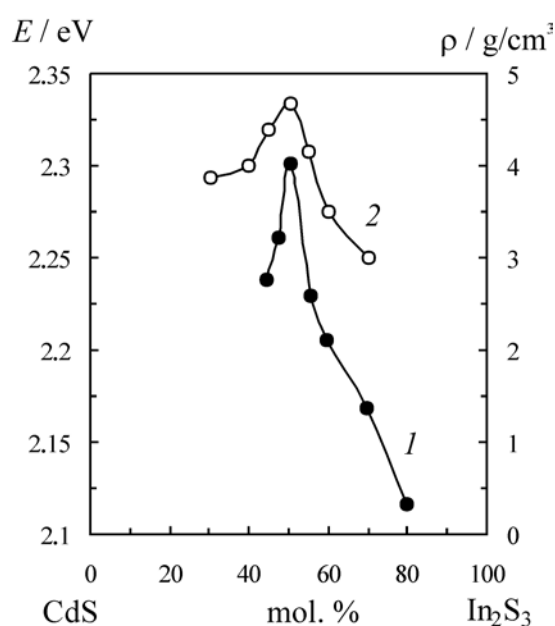
Fig. 5. Concentration dependences of the band gap (*1*) and density (*2*) of films of the CdS–In$_2$S$_3$ system

characteristics of the $CdIn_2S_4$ compound are presented in Table 2.

The range of existence of solid solutions with indium sulphide according to the data of X-ray phase analysis can reach 45 mol% CdS, while with cadmium sulphide it did not exceed 2 mol% In_2S_3. The behaviour of electrical conductivity with a sharp minimum near 2.5 mol% In_2S_3 (Fig. 6) was typical, which definitely indicated the formation of limited solid solutions.

The spectral position of luminescence bands did not depend on the composition of CdS–In_2S_3 films (Fig. 7); the centres of radiative recombinations typical for CdS, apparently, did not change significantly when the bulk composition changed. Only a redistribution of intensities occurred, which can be associated both with

the change in the amount of centres and the redistribution of recombination flows involving these centres [33].

7. CdS–SnS and CdS–SnS$_2$ systems

Redox processes do not occur in the solutions of chlorides of tin (II) and (IV) and thiourea, unlike salts of copper (II) and iron (III). The preservation of the oxidation state of tin allowed obtaining the layers of SnS and SnS_2 sulphides directly using the corresponding chlorides for the synthesis of $[Sn(thio)_2Cl_2]$ and $[Sn(thio)_4]Cl_4$ complexes in acidic (for the suppression of hydrolysis) aqueous solutions. It should be noted that other metals (Ga^{3+}, In^{3+}, Cr^{3+}) require the same method of oxidation to suppress hydrolysis. However, a strongly acidic environment had a negative effect

**Table 2.** Some properties of the $CdMe_2S_4$ compounds deposited in thin layers from the solutions of thiourea coordination compounds

Sulphide	E_g, eV	E_{pc}, eV	E_{pl}, eV	σ, cm/m	ρ, g/cm³	Identification
$CdIn_2S_4$	2.3	2.3	1.53 1.70	$3 \cdot 10^{-2}$	4.7	XRD
$CdBi_2S_4$	1.4	2.1–1.5	–	$3.2 \cdot 10^{-1}$	7.0	XRD
$CdCr_2S_4$	2.1	–	–	$3.6 \cdot 10^{-3}$	4.1	XRD

Designations: E_g is the band gap; E_{pc} is the photoconductivity band; E_{pl} is the photoluminescence band; σ is the specific electric conductivity; ρ is the density.
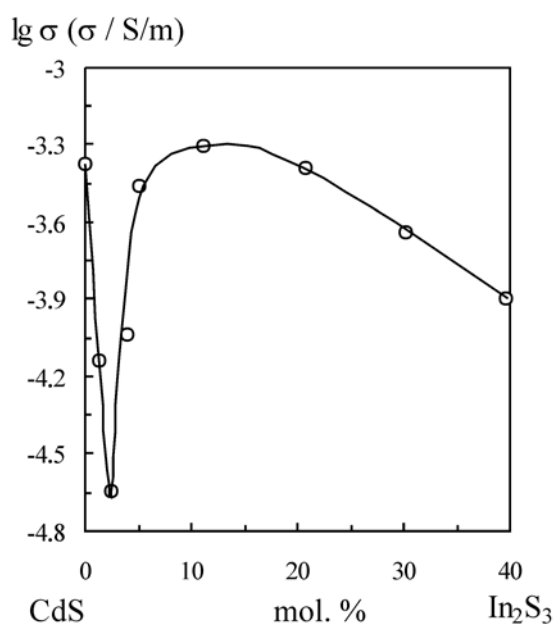
Fig. 6. Dependence of specific electric conductivity of CdS–In_2S_3 films on the composition on the part of CdS
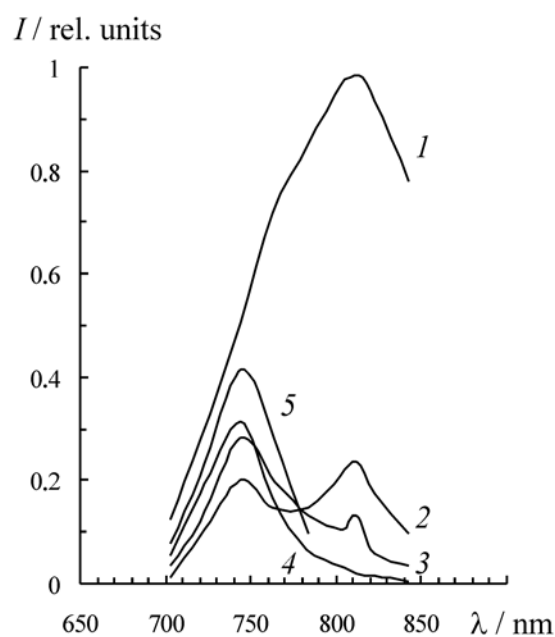
**Fig. 7.** Photoluminescence spectra of films of the CdS–In_2S_3 system: *1* – 0; *2* – 10; *3* – 50; *4* – 90; *5* – 100 mol% In_2S_3

on the formation of coordination compounds due to the S-protonation of the $SC(NH_2)_2$ molecule competing with the formation of complexes. Thus, in order to obtain "cadmium sulphide – tin (II), (IV) sulphides" films, the pH of the solutions was gradually increased in accordance with the growth of the content of tin salts.

The dependence of the band gap on the composition for the CdS–SnS films showed sudden changes near the compositions of 5 and 95 mol% SnS. Specific electric conductivity had the extrema at the same points. Such behaviour of properties may indicate the formation of limited solid solutions. Indeed, XRD showed the existence of solid solutions near CdS and SnS with homogeneity regions no less than 5 mol%. Photoconductive films can be obtained up to the composition of 70 mol% of tin sulphide. The maximum of photosensitivity significantly shifted to the long-wave region from the value of 515 nm typical for intrinsic photoconductivity of pure CdS (E_g = 2.4 eV).

The films of the CdS–SnS$_2$ system are of interest as they contain wide-band semiconductors with similar band gap values ($E_{g(SnS2)}$ = 2.2 eV) that are photosensitive in the visible region of the spectrum. Despite the heterophasic nature of the mixed films, it was possible to obtain the samples with a continuously shifting absorption edge due to the superposition of the spectra of individual phases (Fig. 8). The sharp dependence of the edge position on the composition near pure components indicated their solubility. This was also confirmed by the structure of the absorption spectra that looked like $h\nu\alpha \sim (h\nu - E_g)^{1/2}$ for the compositions in the region of 0–10 mol% SnS$_2$ and $\alpha \sim (h\nu - E_g)^{3/2}$ in the region of 95–100 mol% SnS$_2$. The first one was characterised by cadmium sulphide (direct permitted transition), the second one was characterised by tin sulphide (indirect permitted transition $\Gamma \rightarrow L$).

The concentration dependence of the photosensitivity maximum point E_{pc} correlated with the dependence of the band gap in the regions of solubility of sulphides (Fig. 8). The additions of tin (IV), similar to other heterovalent impurities (Bi), resulted in a short-wave shift of the photosensitivity band of cadmium sulphide. The change in E_{pc} in the region of the equimolar composition may be indicative of a wide homogeneity region of the intermediate phase of
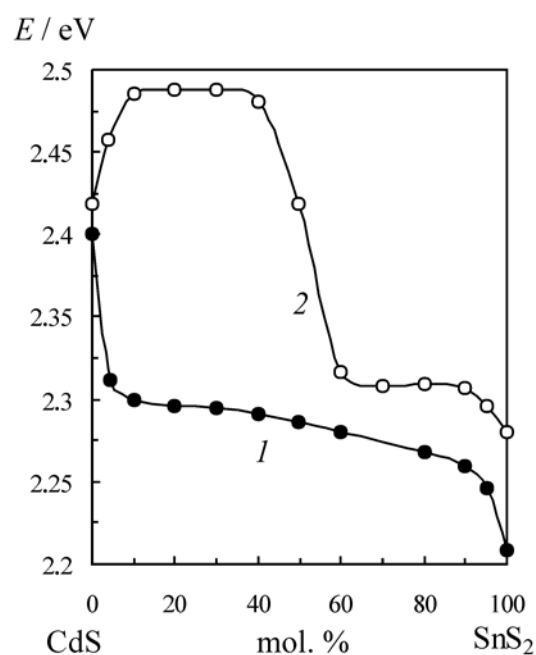

Fig. 8. Dependences of the observed optical band gap (*1*) and spectral position of the photosensitivity maximum (*2*) of CdS–SnS$_2$ films on the composition

the berthollide type, although X-ray phase analysis did not show any certain presence of chemical compounds in the CdS–SnS$_2$ films. This issue requires further investigation.
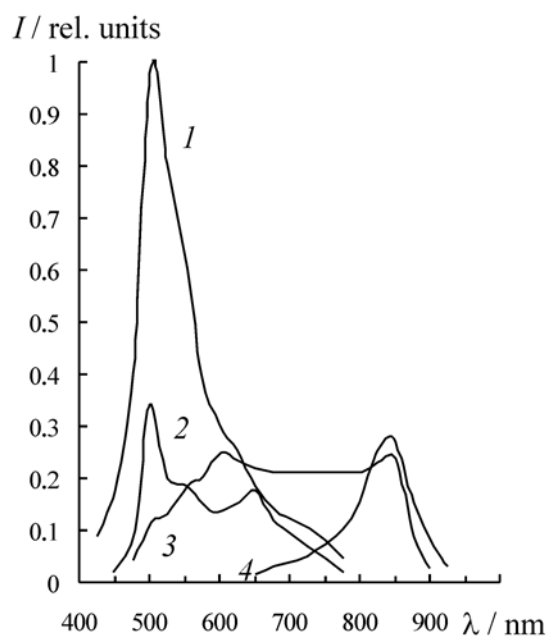
8. CdS–Bi$_2$S$_3$ system

The analysis of the data of X-ray diffraction allowed establishing the existence of a CdBi$_2$S$_4$ compound [34] in the films of the CdS–Bi$_2$S$_3$ system. The properties of the compound are presented in Table 2. It is assumed that cadmium sulphide dissolves in bismuth sulphide through the penetration of cadmium atoms into the interstitial space of the Bi$_2$S$_3$ structure. At the same time, on the part of cadmium sulphide, the most probable mechanism is the replacement of cadmium nodes with the atoms of bismuth. The areas of existence of solid solutions according to the results of X-ray phase analysis and indirect methods were determined by the values of 1 mol% Bi$_2$S$_3$ on the part of CdS and 5 mol% CdS on the part of Bi$_2$S$_3$.

The formation of the only compound in the CdS–Bi$_2$S$_3$ system was confirmed by the existence of maxima on concentration dependences of the properties at coordinates corresponding to the CdBi$_2$S$_4$ composition (Fig. 9). In this case, the extreme behaviour of electric conductivity is
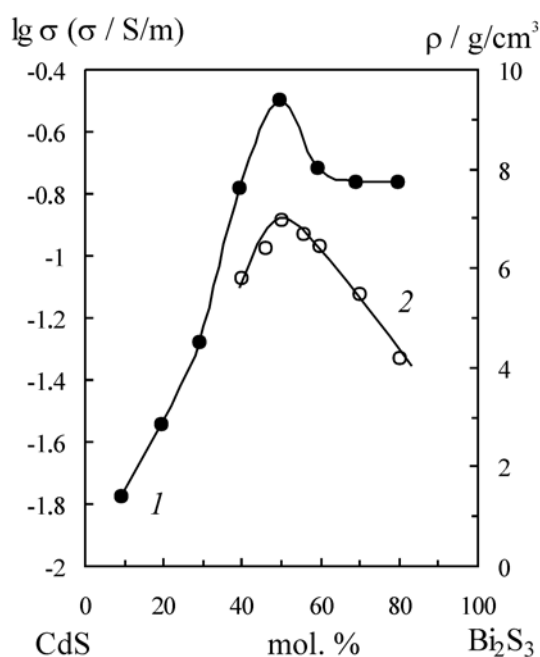
Fig. 9. Concentration dependences of the specific electric conductivity (*1*) and density (*2*) of films of the CdS–Bi$_2$S system

Fig. 10. Photoconductivity spectra of films of the CdS–Bi$_2$S$_3$ system: *1* – 0; *2* – 40; *3* – 50; *4* – 100 mol% Bi$_2$S$_3$

informative when it comes to the identification of a chemical compound, as it is "duplicated" by the specific features of other properties and the data of X-ray phase analysis.

The monotonic dependence of the optical band gap can be associated with the fact that the position of the edge of the fundamental absorption was determined by the most narrow-bandgap semiconductor, especially if there was a great difference between the band gaps. It can be said that the most narrow-bandgap material "masked" the optical properties of the film on the whole. Remarkably, it did not occur, for instance, in case of CdS–In$_2$S$_3$ films as both sulphides composing the film had very close values of bandgap.

The photosensitivity of the CdS–Bi$_2$S$_3$ layers with equimolar composition was considerably different from the photosensitivity of films of other alloys. In this case, the spectral distribution of photosensitivity was characterised by an extended gap (Fig. 10) that, apparently, had a complex structure and consisted of several unresolved bands belonging to the CdBi$_2$S$_4$ compound.

9. CdS–Cr$_2$S$_3$ system

Solid-phase interactions in the thin films of the CdS–Cr$_2$S$_3$ system are similar to the studied

interactions in CdS–Bi$_2$S$_3$ films [35]. This primarily applies to the existence of a compound with the CdCr$_2$S$_4$ composition (Table. 2). We should also take into account similar behaviour of the dependences of film properties on the composition that include experimental points for the composition corresponding to the compound (Fig. 11). A non-specific concentration dependence of the optical band gap can be explained by the fact that the narrow-bandgap chromium sulphide ensured the main absorption by a heterophasic film.

It appeared that the introduction of chromium sulphide created the centres of non-radiative recombination that were rather effective and significantly reduced the lifetime of nonequilibrium carriers. Indeed, when the content of Cr$_2$S$_3$ increased, we observed a very sudden drop in the intensity of the near IR luminescence of CdS, on the one hand, and significant reduction of a photoresponse, on the other hand. The influence of oxygen that was included in the structure of the film and eliminates the distortion of the crystal lattices had an effect on the shift of the photosensitivity maximum to the short-wave region. This effect was evidently related to the increase of ionicity of the bond during the interaction of solid components of a film with oxygen. Nevertheless, in addition to
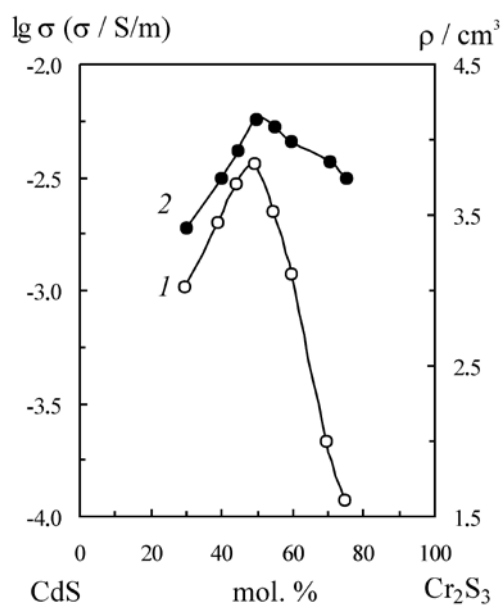
Fig. 11. Concentration dependences of the specific electric conductivity (*1*) and density (*2*) of films of the CdS–Cr$_2$ system

the described reduction of intensity, we can also note a shift of the luminescence band in near IR region that indicates the solubility of chromium sulphide in cadmium sulphide.

10. CdS–FeS$_2$ system

As it was noted before, partial reduction of Fe^{3+} to the oxidation state of Fe^{2+} occurred in solutions of iron (III) salts in the presence of thiourea. This process led to the deposition of iron sulphides FeS and FeS$_2$ depending on the composition of the initial solution and the temperature of the substrate. The conditions were found (the temperature of the substrate 300 °C, 4x and more excess of thiourea in relation to the ferrous salt (FeCl$_3$)) for the release of a phase of pyrite FeS$_2$ that is rather perfect in structure and its optical and electric properties.

There was no significant solubility in the CdS–FeS$_2$ system neither on the part of CdS or on the part of FeS$_2$. The luminescence intensity typical for cadmium sulphide decreased sharply as soon as small amounts of iron were added. Unlike the additions of Cr^{3+}, there was no shift in the bands in the luminescence spectra.

The concentration dependence of specific electric conductivity of films with an expressed

maximum at the ratio of the components CdS:FeS$_2$ = 1:2 apparently cannot clearly indicate the presence of the compound due to the reasons mentioned above (CdS–Ag$_2$S system). The results of the X-ray phase analysis allowed stating with greater certainty that no compounds were formed in the CdS–FeS$_2$ system. Therefore, the CdS–FeS$_2$ system is an example of almost total lack of interaction between the components.

11. Conclusion

The possibility to obtain solid solutions and chemical compounds of sulphides in the process of deposition considerably enriches the ASP method. The studied systems showed almost all types of interactions, and the formation of compounds with cadmium sulphide was typical for sulphides of Me$_2$S$_3$ metals of groups III, V, and VI. The formation of solid solutions with CdS was established almost in all systems, although mutual solubility was low for sulphides of metals of groups I (Ag) and VIII (Fe). The greatest range of the area solid solutions was observed in the CdS–In$_2$S$_3$ system where the solubility of cadmium sulphide in In$_2$S$_3$ reached the value of 45 mol%.

Therefore, it was possible to vary the properties of films using specific features of solid solution interactions of sulphides. Photoluminescence of the layers based on CdS allowed observing the ways of controlling a certain property (Table 3). There are possibilities for the activation of luminescence and shift of the bands as well as for the change of intensities of the bands without changing their spectral position.

When interpreting the mechanism of formation of solid solutions and compounds of sulphides, it should be taken into account that multicore thiourea complexes with dissimilar cores were not found in the solutions with various complexing agents. This indicates an independent existence of complexes in the solution, although we cannot make assumptions about their independent thermal decomposition within the use of ASP method. The conditions of the deposition of films did not involve a direct solid-phase interaction of the released sulphides with the formation of solid solutions and chemical compounds. The lowest threshold of deposition temperatures was determined by the temperature of decomposition of the most thermally stable TCC and did not exceed 250 °C. Diffusion coefficients in solids

Table 3. The nature of the photoluminescence spectra of films of the CdS–Me$_m$S$_n$ systems

Activation of cadmium sulphide luminescence with small additions of an activator metal	CdS – Cu$_{2-x}$S, CdS – MnS
Continuous shift of the band in the whole range of compositions 0–100 mol%	CdS – ZnS
Continuous shift of the band, probably, within the limited range of solubility	CdS – Cr$_2$S$_3$
Two luminescence bands with a variable ratio of intensities	CdS – In$_2$S$_3$
"Quenching" of luminescence	CdS – Cr$_2$S$_3$, CdS – FeS$_2$

were low at such temperatures. If metal sulphides were released independently during the thermal destruction of complexes, solid-phase interactions of most sulphides could not be realised. Therefore, the interaction occurred at the moment of thermal destruction of complex compounds right on the substrate due to the emerging valence opportunities of their structural fragments.

Author contributions

Semenov V. N. - scientific leadership, research concept, conducting research and methodology development, writing of text, final conclusions.

Naumov A. V. - research concept, conducting research and methodology development, writing of text, final conclusions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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