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TECHNOLOGY FOR OBTAINING NANOFILMS OF VARIOUS METALS BY CHEMICAL DEPOSITION IN THE FORM OF SULFIDES AT LOW TEMPERATURE

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Abstract: *This paper presents the results of research on the topic "Development and implementation of technologies for obtaining semiconductor, photosensitive and fluorescent nanomaterials based on the processes of directed synthesis of metal sulfides from unitiolate coordination compounds". This paper considers the growth of nanocrystals on a multicomponent silicate glass in which the semiconductor phase, with a concentration of approximately 1%, was dissolved during synthesis. During secondary heat treatment of glass samples, nucleation and growth of semiconductor nanocrystals occurs as a result of diffusive phase decomposition of a supersaturated solid solution.*

Key words: *unithiolate complex, sulfides, semiconductors, crystal lattice defects, bandgap, sodium 2, 3-dimercaptopropanesulfonate, crystal lattice energy, thermolysis*

ТӨМЕН ТЕМПЕРАТУРАДА СУЛЬФИД ТҮРІНДЕ ХИМИЯЛЫҚ ТҰНДЫРУ ӘДІСІМЕН ӘРТҮРЛІ МЕТАЛДАРДЫҢ НАНОҚАБЫРШЫҚТАРЫН АЛУ ТЕХНОЛОГИЯСЫ

Аңдатпа: *Бұл мақалада «Унитиолатты координациялық қосылыстардан металл сульфидтерінің бағытталған синтезі процестерінің негізінде жартылай өткізгішті, фото сезімтал және люминесцентті наноматериалдарды алу технологияларын әзірлеу және іске асыру» тақырыбы бойынша зерттеу нәтижелері берілген. Жұмыста көп компонентті силикатты шыныда нанокристалдарды өсіру қарастырылады, онда жартылай өткізгіш фазасы, концентрациясы шамамен 1% синтезде ерітілген. Шыны үлгілерді екінші рет термиялық өңдеу кезінде жартылай өткізгіш нанокристалдардың түзілуі мен өсуі қайта қанықтырылған қатты ерітіндінің диффузиялық фазалық ыдырауы нәтижесінде болады.*

Түйінді сөздер: *унитиолатты кешен, сульфидтер, жартылай өткізгіштер, кристалдық тордың ақаулары, тыйым салынған аймақтың ені, 2,3 натрий димеркаптопропансульфанаты, термолиз*

ТЕХНОЛОГИЯ ПОЛУЧЕНИЯ НАНОПЛЕНОК РАЗЛИЧНЫХ МЕТАЛЛОВ МЕТОДОМ ХИМИЧЕСКОГО ОСАЖДЕНИЯ В ВИДЕ СУЛЬФИДОВ ПРИ НИЗКОЙ ТЕМПЕРАТУРЕ

Аннотация: *В данной статье представлены результаты исследования по теме «Разработка и реализация технологий получения полупроводниковых, фоточувствительных и люминесцентных наноматериалов на основе процессов направленного синтеза сульфидов металлов из унитиолатных координационных соединений». В работе рассматривается выращивание* *нанокристаллов на многокомпонентном силикатном стекле, в котором полупроводниковая фаза концентрации приблизительно 1% была растворена в течение синтеза. При вторичной термической обработке стеклянных образцов, зародышеобразование и рост полупроводниковых нанокристаллов происходит в результате диффузионного фазового разложения пересыщенного твердого раствора.*

Ключевые слова: *унитиолатный комплекс, сульфиды, полупроводники, дефекты кристаллической решетки, ширина запрещенной зоны, 2,3 димеркаптопропансульфанат натрия, термолиз*

Introduction

It is common knowledge that until now mainly semiconductor materials are still synthesized at high temperature. The strict observance of the temperature range is not disadvantage of this method, but the slightest change in temperature leads to structural changes and, accordingly, to changes in the properties of semiconductor materials. In this work, under the guidance of Professor Kh.K. Ospanov, an original new low-temperature method of unithiolate coordination compounds thermolysis is proposed [1].

It should be noted that at one time a whole series of unithiolate metal complexes was synthesized at the Department of Physical Chemistry and Electrochemistry of Al-Farabi Kazakh National University under the guidance of Professor Kh.K. Ospanov. The results of systematic experimental studies of the chemical and physical properties of these compounds over the last 30 years allow to predict the biological activity presence with a high level of probability. One of the authors later successfully used this developed methodology of synthesis in the form of sulfides from unithiolate metal complexes for the synthesis of semiconductor materials at low temperature with specified properties [2, 3].

Prospectivity of an aerosol pyrolysis method consists in simplicity of obtaining of material semiconductors, mixed layers on their basis, introduction of active impurities in one technological mode with simultaneous formation of electric supply contacts in a single cycle. This method allows to realize the serial and economical profitable production process for deposition of sulfide films of many metals with unique properties and makes it possible to significantly extend the range of application of the useful properties of these semiconductor materials of various purposes (as a battery source allowing to obtain solar energy). Therefore, the search for a scientifically grounded approach and a method for the synthesis of semiconductor materials with the same properties at a low temperature by a non-traditional method is very relevant [1]. The essence of this method consists of the fact that, on the basis of establishment of thermodynamic and kinetic regularities of the decomposition process of some metals coordination compounds with sodium 2,3-dimercaptopropanesulfonate (unithiol), it is possible to obtain result in the form of sulfides at low temperature with stable properties.

More details about the prospects and importance of this work of thermal decomposition of unitiolate metal complexes using various physical methods were studied together with the staff of the «National nanotechnology laboratory of open type» at al-Farabi Kazakh National University under the guidance of the state prize winner, Professor M.T. Gabdullin.

For us it was of great interest to find out that the sulfides of CdS and ZnS and their binary compounds will possess semiconductor properties [4-7].

Experimental Part

The methodology of preparation and synthesis of complex cadmium and zinc compounds separately and their binary compounds consists in the fact that different solutions of cadmium and zinc unithiolate complex (binary compound) were used for synthesis of the cadmium and zinc unithiolate complex in various ratios using only reagents of special purity.

Synthesis of CdSxZnSy binary compounds in various ratios in the form of a film on glass was performed to select the most effective semiconductor materials. The following composition of the complexes was prepared:

Cd^{2+}+Un2=1:2
CdUn2:ZnUn =1:1
CdUn2:ZnUn =1:0,9
CdUn2:ZnUn=1:0,7
CdUn2:ZnUn2=1:0,5
CdUn2:ZnUn2 =1:0,3
CdUn2:ZnUn2 =1:0,1
and conversely: Zn^{2+}+Un2=1:2
ZnUn2:CdUn2= 1:0,1
ZnUn2:CdUn2= 1:0,3
ZnUn2:CdUn2= 1:0,5
ZnUn2:CdUn2=1:0,7
ZnUn2:CdUn2= 1:0,9
ZnUn2:CdUn2= 1:1

The synthesis of cadmium and zinc sulfide films in a different percentage of unithiolate complex compounds on dielectric substrates, as well as on semiconductor substrates is performed. For the synthesis of CdSxZnSy binary compounds, in the form of a film on glass, solutions with a different percentage of cadmium and zinc sulfides, namely 0%, 10%, 30% to 50%, 70%, 90%, 100% cadmium, were chosen.

The optical characteristics of cadmium sulfide and zinc sulfide films in a different percentage ratio obtained by thermolysis from unithiolate complex compounds were studied. Synthesis of CdSxZnSy binary compounds in various ratios in the form of a film on glass was performed to select the most effective semiconductor materials.

The cadmium and zinc sulfides thin layers' formation by the aerosol pyrolysis occurs under non-equilibrium conditions affecting formation of a less perfect structure as compared to lump samples. This is indicated by several underestimated values of the film density and the calculated values of the current carriers' mobility.

The types of films of cadmium sulfide and zinc sulfide and CdSxZnSy binary compounds are studied with different physical methods, as well as the properties of cadmium sulfide and zinc sulfide films synthesized from unithiolate complexes for use as a battery for solar energy obtain.

The active alloying additives introduction makes it possible to significantly increase the photocurrent multiplicity, the luminescence intensity, and shift the maximum value of these parameters to a given area. This process is interesting from the point of view of solid-phase interactions. Thus, according to luminescence analysis solid solutions with cation substitution Cu+Me are formed when alloying of zinc sulfide or cadmium sulfide films with copper ions during spraying of solutions at low concentrations (up to 1-10-2 atomic % of Cu). An interstitial solid solution is formed in the layers with a higher content of copper ions, and the interstitial atoms concentration being insignificant, since an independent Cu_2S phase begins to be released at CCu ~1*10-1 mol/L. After the substitutional solid solution formation, not only Cu+i, but also Oxi is formed. When the distance between these defects becomes sufficiently small, the following interaction occurs:

$$Ox_i + 2\ Cu+_i + 2e^- \rightarrow Cu_2O$$

On the one hand, this contributes to cleaning the films from oxygen throughout the entire volume, and on the other hand, to secrete it on dislocations in the form of an oxide phase. The method used for films deposition makes it possible to considerably expand the area of solid-phase solubility in the anion sub lattice as compared to lump samples. For example, according to X-ray fluorescence spectroscopy, the chlorine and bromine solubility in the layers of cadmium sulfide is, respectively, 1.76 and 1.75 mol. %.

Complex compounds with the necessary complexing agents of cadmium and zinc are introduced into the spray solution for solid solutions deposition with cationic substitution. Solid-phase interactions were studied in 13 ternary systems based on cadmium sulfide with cationic substitution. The composition-property diagrams construction together with

X-ray diffraction analysis allowed to establish that limited solubility is fixed for most thin-film compositions, and continuous solid solutions are formed for the CdS-ZnS system. At the same time, as follows from X-ray phase analysis data, the wurtzite structure typical for CdS deposited from [CdUn2Cl2] changes into sphalerite (ZnS) in the CdS-ZnS system at a zinc sulfide concentration of 65 mol. %. Concentration dependences of the bandgap and the luminescence maximums position confirm conclusion that a continuous series of solid solutions is formed in this thin-film system. Layers of equimolar composition have the maximum luminescence intensity, as shown in Figure 2.

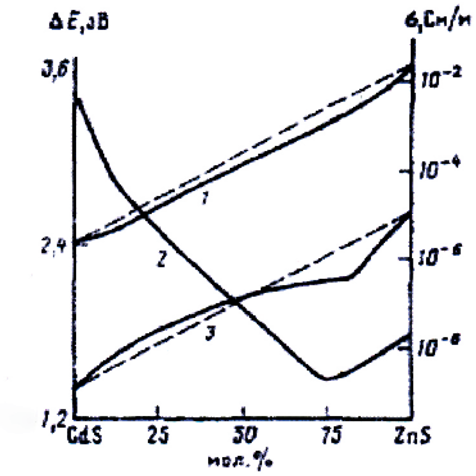

Figure 1 – Dependence of the bandgap (1), specific electrical conductivity (2) and the position of the luminescence maximum values (3) on the $Cd_xZn_{1-x}S$ films composition

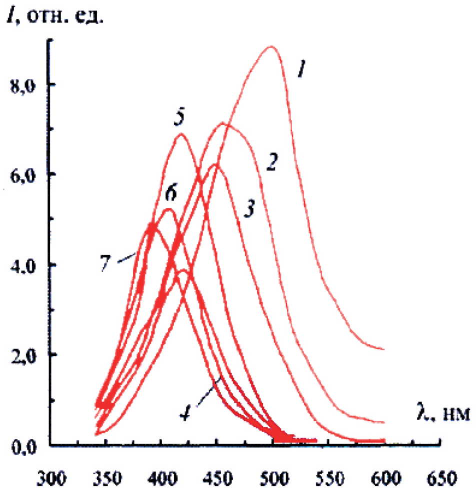

Figure 2 – Luminescent spectrum of CdxZn1-xS films

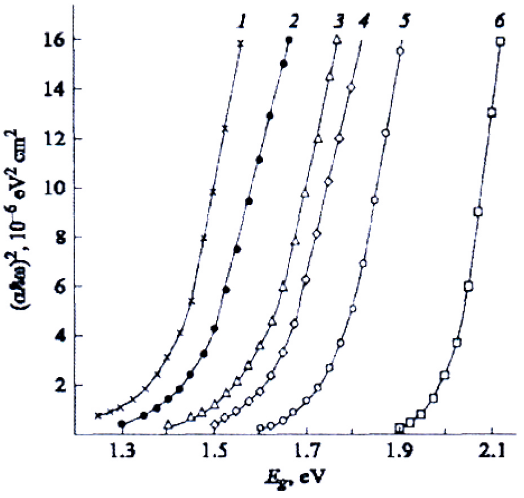

Figure 3 – Concentration dependence of the specific electrical conductivity and bandgap of the CdS-ZnS system photosensitivity maximum values

The results of X-ray phase analysis of CdS – In2S3 films indicate the existence of CdIn2S4 chemical compound with a spinel structure, as well as the solid solutions formation based on ZnS in the concentration range of 0-45 mol. % of CdS. The length of solid solutions based on cadmium sulfide is small and amounts to 2 mol. % of ZnS (Figure 3).

It is shown that in CdS – Me2S3 systems, the heterovalent substitution occurs in formation of solid solutions based on the cadmium sulfide structure:

$Me2S3 = 2\ Me_{Cd} + 3SxsV//Cd$

(→CdS)

but on the basis of the structure of the trivalent metal sulfide:

$2\ CdS = 2\ Cd/Me\ 2S^{x}_{s} + V_{s}$

According to the quasi-chemical reaction, cadmium vacancies are formed in the solid solutions formation, and in accordance with the sulfur vacancy. There is an excess of sulfur atoms in the inner sphere of the complex through which the ligand is coordinated since the process of film deposition occurs through unithiolate complexes formation stage with a coordination number equal to 4 for Cd^{2+} and for Me^{3+}.

The cadmium vacancies presence (Table 1) makes it difficult to form solid solutions by reaction. The results of experimental studies have shown that the chemical compounds and solid solutions formation based on binary compounds is also observed in CdS-ZnS and $Cd_xZn_{1-x}S$ thin-film systems. Layered phases are formed in CdS-ZnS system due to the cadmium sulfide introduction into the interband space of the ZnS structure [1,8].

Table 1. Nature of optically active centers and prevailing defects in zinc sulfide and cadmium sulfide samples obtained from unithiolate coordination compounds

Luminophore	ZnS		$Cd_{0.5}Zn_{0.5}S$	CdS	
	λ,nm E, eV	type of defect	λ,nm E, eV	λ,nm E, eV	λ,nm E, eV
Dark blue	440-470 2,80-2,64	$V_{Zn//'}$, $(V_{Zn}Cl_S)$	-	-	-
Blue	-	-	528 2,35	-	-
Green	520-530 2,38-2,34	$(V_{Zn}O_S)$	556 2,23	515-540 2,1-2,3	E_g
	545-565 2.28-2.19	$(V_{Zn}O_i)$	571 2.17	-	-
Orange			640 1,94		
			643 1,93		
	-	-	680 1,82	-	-
Red	-	-	-	-	-
	-	-	-	730 1,7	-
	-	-	722 1,72	780 1,59	-
Infrared	-	-	810 1,53	810 1,53	-

The bandgap, specific resistivity and the photosensitivity are determined. A comparative evaluation of cadmium and zinc sulfides synthesized from their unithiolate complexes as an effective semiconductor material was performed (Fig. 1-3).

As shown in Table 2, the values of synthesized binary compounds of unithiolate complexes of cadmium and zinc CdS:ZnS cadmium and zinc sulfides from CdUn2:ZnUn2=1:0.5; CdS:ZnS from CdUn2:ZnUn2 =1:0.3; CdS:ZnS from CdUn2:ZnUn2 =1:0.1; have lower values compared to CdS and ZnS synthesized separately. Consequently, we can assume from the bandgap value that CdS and ZnS synthesized binary compounds have effective semiconductor properties (Fig. 1, 3). They are prospective for solar energy obtain.

Table 2. The bandgap values of synthesized binary compounds of unithiolate complexes of cadmium and zinc CdS:ZnS cadmium and zinc sulfides from $CdUn_2$:$ZnUn_2$=1:0.5; CdS:ZnS from $CdUn_2$:$ZnUn_2$ =1:0.3; CdS:ZnS from $CdUn_2$:$ZnUn_2$ =1:0.1

Binary compounds of cadmium and zinc	The bandgap, eV
CdS	**2,2**
CdS:ZnS from $CdUn_2$:$ZnUn_2$=1:0,5	1,6
CdS:ZnS from $CdUn_2$:$ZnUn_2$ =1:0,3	1,5
CdS:ZnS from $CdUn_2$:ZnUn2 =1:0,1	1,3
ZnS	**3,6**

According to the conducted studies, the solid-phase product - metal sulfide formation is mainly determined by the nature of the complexing agent, while the nature of the volatile by-products of thermolysis depends on the nature of the coordinated and outer-sphere anions.

The growth rate is limited by the unithiolate cadmium complexes decomposition rate. The deposition process is limited to transporting unithiolate cadmium complexes to the substrate surface in a range where the epitaxy rate is sufficiently high. We assume that these molecules mainly decompose near the surface due to a sufficiently high temperature gradient. The rate of integration is comparable with the rate of evaporation into vacuum.

The unithiolate cadmium complex decomposition products can also shift from the surface to the convective stream of diffusion hydrogen through the same near-surface layer through which the unithiolate cadmium complexes diffuse to substrate surface. At higher temperatures, unithiolate cadmium complexes can decompose not reaching the substrate surface. In this case, the decomposition products shall overcome the remaining near-surface layer by diffusion before reaching of the substrate surface. This slows down the integration process of the original molecules into the crystal lattice and increases probability of their escape into convective stream. In the general case, not all molecules reached the surface of the growing film are integrated into the crystal lattice sites. A part of molecules returns to the vapor phase. The molecules transportation is presumably mainly limited by diffusion through a thin (about 1 mm thick) near-surface laminar layer of hydrogen gas. The original components and reaction products are sufficiently well mixed above this layer due to convection.

It was found experimentally that rate decreases at the final stage of film growth and, ultimately, growth stops at all («effect of growth saturation»). This can be related to the sulfide re-evaporation and taken into account by introduction of a new part of the reflected stream.

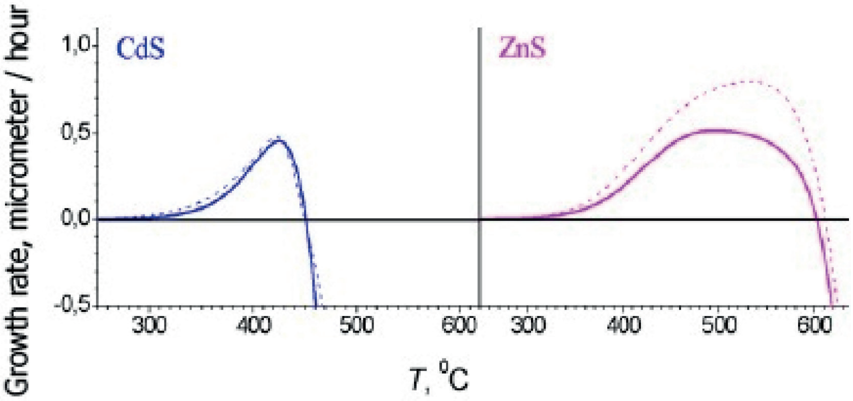

Figure 4 – Comparison of calculated (dashed curves) and experimental (solid curves) temperature dependences of the growth rate for ZnS and CdS compounds

Synthesis of semiconductor compounds in a dielectric matrix, in addition to crucially important possibility of obtaining of crystals of microscopic dimensions has one more advantage. Indeed, since the crystalline phase concentration in the matrix is relatively small, it is possible to directly record the absorption spectra of crystals on relatively thick samples obtained by mechanical polishing. Thus, such heterogeneous glasses are a new, extremely convenient object for investigation of dimensional effects in semiconductors.

Also, the microcrystals growth on multicomponent silicate glass is viewed, where a semiconductor phase with concentration about 1% was dissolved during the synthesis. In the secondary heat treatment of glass samples, the nucleation and growth of semiconductor microcrystals occurs as a result of the diffusion phase decomposition of the supersaturated solid solution. An experimental dependence of the mean radius of the CdS microcrystal as a function of the heating time for a number of temperatures has been established. The value of mean radius of the microcrystal for the sample was determined by the method of small-angle X-ray scattering in the spherical particles approximation.

The stage of recondensation growth is characterized by a stationary (steady state) condition of the size distribution not depending on the initial conditions, and an analytical expression was obtained for this distribution. This expression actually describes the size distribution of semiconductor particles grown according to the reviewed method. This fact allows take into account the microcrystals sizes dispersion in the quantitative analysis of the experimental results reviewed in this section.

Also, CdS nanoparticles were prepared by rapid mixing [1] of aqueous solutions of cadmium sulfate (extra pure grade) with unithiol (extra pure grade) at room temperature. The correlation dependence usage between the threshold absorption wavelength and the crystallite diameter allowed to obtain the estimated values of mean particle (Fig. 2). They have values close to 5 nm and to 3 nm, respectively. It should be noted here that presence in the spectrum of a sufficiently well-resolved exciton peak at 360 nm can serve as indication of a relatively narrow particle size distribution in solutions stabilized with gelatin. This peak becomes less expressed at a higher concentration of CdS, additional absorption in the area of 370-450 nm and the band edge occurs. The band edge is characterized by a maximum value at 360 nm, since it shifts to the long-wavelength side. All this testifies that there are also larger formations along with the particles to which the spectrum 3 belongs.

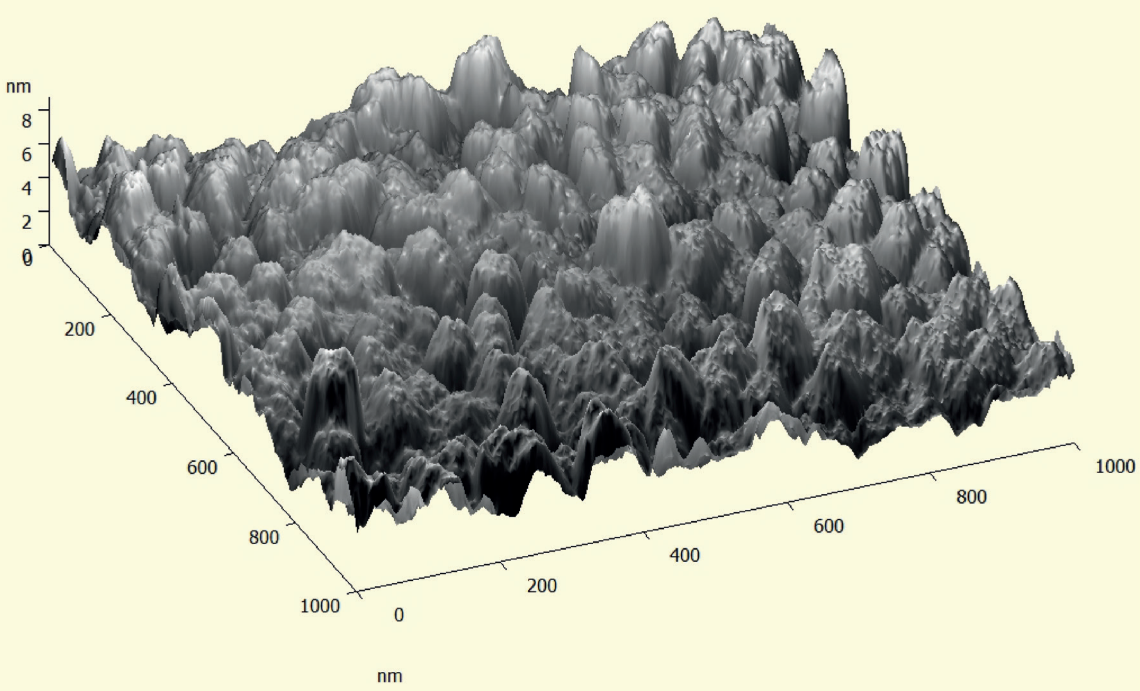

Figure 5 – Surface image of one of the x-film samples obtained with an atomic-force microscope

As shown in Figure 5 the surface image of one of the x-film samples obtained with an atomic-force microscope shows that the surface roughness ranges from 2 nm to 8 nm. All samples have the same morphology in the form of uniformly distributed crystallites of different diameters over the sample surface.

When studying crystallites on the surface of the film, it was found that clusters with a diameter of about 65 nm belong to the maximum population.

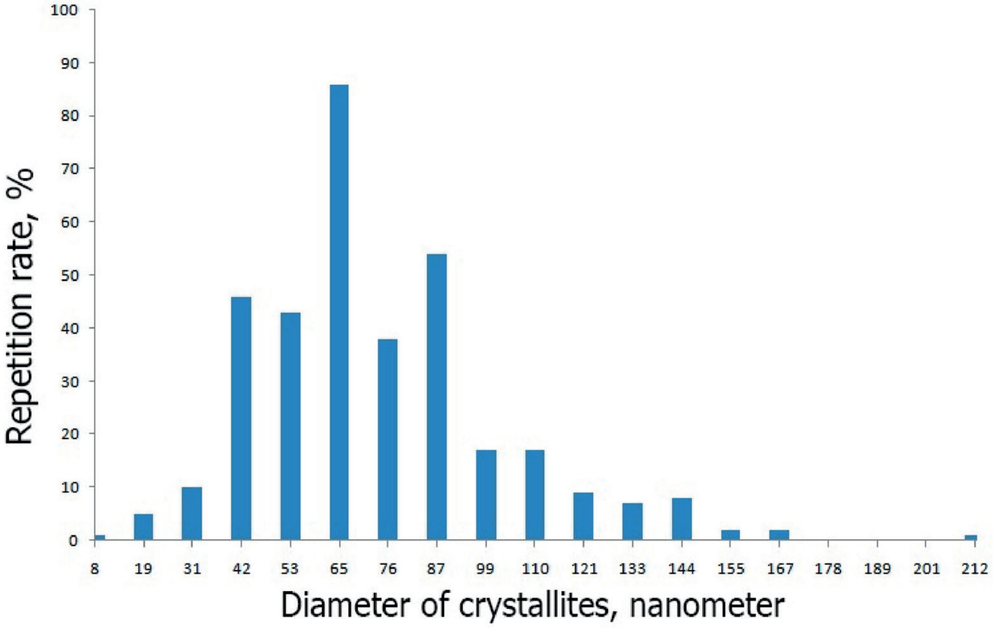

Figure 6 – Distribution of the crystallites concentration depending on their diameter

The crystallites concentration distribution depending on their diameter was calculated using static analysis methods (Fig. 4). The maximum number of clusters accrues to size of 65 nm, but there are 2 more maximum values at 42 nm and 87 nm within distribution, and the tails extend from 8 nm (probe sensitivity limit) to 212 nm (limit of the scanning range and the subsequent mathematical processing of an image)

Experimental laboratory tests of the developed technologies, obtained new nanostructured materials on the basis of thermal destruction of unithiolate metal complexes in the laboratory of Institute of Physics and Technology were performed. The most prospective ways of practical application of these materials are indicated.

Conclusion

– For the first time semiconductor materials were synthesized at low temperature using a non-traditional method based on the unithiolate complex of cadmium and zinc, in various ratios in order to prepare CdSxZnSy binary compound. The synthesis of cadmium and zinc sulfides films in a different percentage was also performed from unithiolate complex compounds on semiconductor substrates.

– The bandgap, specific resistivity and the photosensitivity are determined. A comparative evaluation of cadmium and zinc sulfides as an effective semiconductor material was performed. The bandgap for CdSxZnSy binary compounds varies from 1.3 to 2.2 electronvolt.

– The studied physical properties of binary compound films in various ratios of cadmium and zinc sulfides synthesized from unithiolate complexes characterize as the battery source for solar energy obtain.

– The measurement of the optical bandgap (Eg), specific electrical conductivity (σ), pycnometric specific gravity (p), the positions of the photoconductivity maximum values (Eps), photoluminescence (Epl) of films of chloride unithiolate complex compounds of cadmium and zinc sulfides showed that they have bright expressed by semiconductor properties.

This technology proposed by the authors for obtaining nanofilms of various metals by chemical deposition in the form of sulfides at low temperature is also used to produce nanofilms of nickel, cobalt and copper sulfides.

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