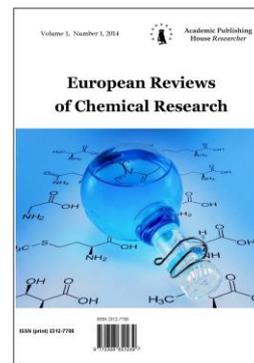


Copyright © 2016 by Academic Publishing House *Researcher*



Published in the Russian Federation  
European Reviews of Chemical Research  
Has been issued since 2014.  
ISSN: 2312-7708  
E-ISSN: 2413-7243  
Vol. 7, Is. 1, pp. 4-9, 2016

DOI: 10.13187/erchr.2016.7.4  
[www.ejournal14.com](http://www.ejournal14.com)



## Articles and Statements

UDC 544.72.05

### Hydrochemical Deposition of $\text{Cu}_2\text{S}$ Films Using Thiocarbamide

<sup>1</sup> Irina A. Glukhova

<sup>2</sup> Larisa N. Maskaeva

<sup>3</sup> Vyatcheslav F. Markov

<sup>4</sup> Stanislav S. Tulenin

<sup>5</sup> Anna I. Shemyakina

<sup>1</sup> Ural Federal University named after the first President of Russia B.N. Yeltsin, Russian Federation  
620002 Ekaterinburg, Mira Str., 19

E-mail: [anutan145@mail.ru](mailto:anutan145@mail.ru)

<sup>2</sup> Ural Federal University named after the first President of Russia B.N. Yeltsin, Russian Federation  
620002 Ekaterinburg, Mira Str., 19

D. Sc. (Chemical), Professor

E-mail: [mln@ural.ru](mailto:mln@ural.ru)

<sup>3</sup> Ural Federal University named after the first President of Russia B.N. Yeltsin, Russian Federation  
620002 Ekaterinburg, Mira Str., 19

D. Sc. (Chemical), Professor, head of the department of physical and colloidal chemistry.

E-mail: [v.f.markov@ustu.ru](mailto:v.f.markov@ustu.ru)

<sup>4</sup> Ural Federal University named after the first President of Russia B.N. Yeltsin, Ekaterinburg,  
Russian Federation

620002 Ekaterinburg, Mira Str., 19

E-mail: [stast1989@mail.ru](mailto:stast1989@mail.ru)

<sup>5</sup> Ural Federal University named after the first President of Russia B.N. Yeltsin, Russian Federation  
620002 Ekaterinburg, Mira Str., 19

E-mail: [anutan145@mail.ru](mailto:anutan145@mail.ru)

#### Abstract

Hydrochemical deposition of the films of stoichiometric composition  $\text{Cu}_2\text{S}$  was determined in ammoniac and acetated layer systems by energy-dispersive elemental analysis. The film composition almost corresponds to formula unit  $\text{Cu}_2\text{S}$ . Electron-microscopic research of the film morphology showed that the particles, which are formed the films of  $\text{Cu}_2\text{S}$  have average size ~10 nm.

The authors conclude that:

1. Nanocrystal films of copper (I) sulfide with the thickness  $100 \pm 10$  nm exhibiting good adhesion to sital substrate were obtained by hydrochemical deposition in systems « $\text{CuSO}_4 - \text{NaAc} - \text{CS}(\text{NH}_2)_2$ » and « $\text{CuSO}_4 - \text{NH}_3 - \text{CS}(\text{NH}_2)_2$ ». EDX analysis confirmed that at hydrochemical deposition the formation of thin  $\text{Cu}_2\text{S}$  film phase which is closed to stoichiometric composition

with the average content of metal and sulfur 66.59 and 33.41 at.%, 66.82 and 33.18 at.% in acetated and ammoniac systems correspondingly occurs.

2. Morphology of obtained films  $\text{Cu}_2\text{S}$  was studied by electron-microscopic research, their nanocrystal nature was determined.

**Keywords:** hydrochemical deposition, thin films, copper (I) sulfide, surface morphology, raster electron microscopy.

### Introduction

Different methods of production of copper (I) sulfide layers are known: solid phase reaction [1], pyrolysis [2, 3], sputtering [4], photochemical method [5, 6], chemical deposition from aqueous solutions [7, 8], vacuum vaporization [9]. Method of synthesis has a significant influence on the variety of film phase states: from  $\text{Cu}_2\text{S}$  to  $\text{CuS}_2$  [10], and therefore – on the structure and morphology of their surface.

As it was shown in our previous paper [11] the advantage of copper (I) sulfide hydrochemical deposition is that it allows to control the changes of the fraction of free metal ions in the reaction mixture by using ligands with different strengths for copper. The control of both copper complex degrees in the solution and process temperature gives an opportunity to vary the characteristics of growing films of  $\text{Cu}_{2-x}\text{S}$ : elemental composition, microstructure, and size of particles, their electrical and optical properties.

It is known that hydrochemical deposition of metal sulfide layers is based on interaction of metal salts in alkaline with chalcogenizer that is usually thiocarbamide or its compounds [12]. Earlier chemical deposition of  $\text{Cu}_2\text{S}$  from aqueous solutions by thiocarbamide  $\text{CS}(\text{NH}_2)_2$  was described in [13-18], as well as by sodium thiosulphate  $\text{Na}_2\text{S}_2\text{O}_3$  in [19, 20] in alkaline [13-17, 19] or in acid [18, 20].  $\text{CuCl}_2$  or  $\text{CuSO}_4$  were used as copper (II) salt. In [18] the function of the complexing agent belonged to tartaric acid  $\text{C}_4\text{H}_6\text{O}_6$ . However, it should be mentioned that the common ligands for copper ions used by scientists are ammonia  $\text{NH}_3$  and triethanolamine  $\text{C}_6\text{H}_{15}\text{NO}_3$  [13-17, 19]. In [11] we showed that the use of complexing agents with different strengths and denticity has a great influence on deposition process rate and morphology features of thin zinc sulfide films formation.

Taking into account the information mentioned above the present article is about elemental composition and morphology of hydrochemically deposited copper sulfide films.

### Experimental

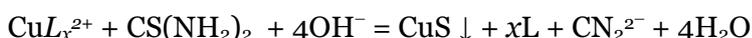
Synthesis of copper sulfide films by hydrochemical deposition was made using two compound variants containing copper sulphate  $\text{CuSO}_4$  as the metal source, and thiocarbamide  $\text{CS}(\text{NH}_2)_2$  as the chalcogenizer. To slow down the rate of sulfide formation ammonia  $\text{NH}_3$  was introduced (ammoniac reaction system) in one case and sodium acetate was introduced (acetated reaction system) in another case. The synthesis of copper sulfide layers in ammoniac mixture was carried out at temperature 298 K in the course of 120 min, in acetated mixture – at 343 K in the course of 45 min. Previously defatted ST-50 sital sheets were used as substrates.

Film thickness was measured with *Linnik MII-4M interferometer*.

Surface morphology and elemental composition study of films were examined with *Scanning Electron Microscope JEOL JSM-5900LV* by Raster (Scanning) Electron Microscopy (REM) with an EDX attachment for X-Ray Spectral Electron Microprobe Analysis.

### Results and discussions

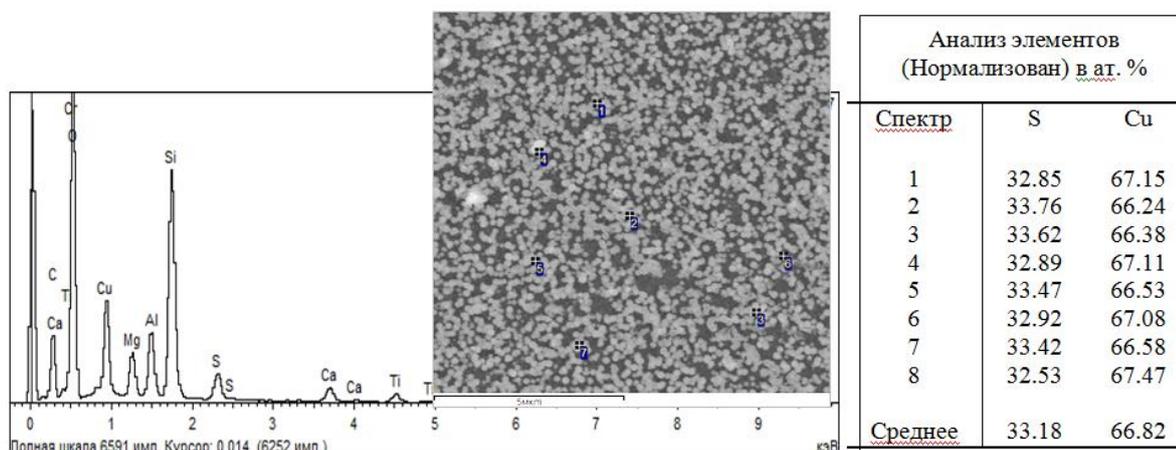
It is believed that during mixture interaction of copper sulphate  $\text{CuSO}_4$  solution and complexing agents  $L$  ( $\text{NH}_3$ ,  $\text{Ac}^-$ ) with thiocarbamide the following reaction of the formation of  $\text{CuS}$  occurs:



It should be noted that in the system it is possible either complete or incomplete reduction of Cu (II) to monovalent state by thiocarbamide having rather high reduction potential (-0.42V) [21, 22].

The result of hydrochemical deposition in both systems was copper sulfide films with thickness 100-110 nm with homogeneous covering of the substrate surface. Copper is in a monovalent state in them.

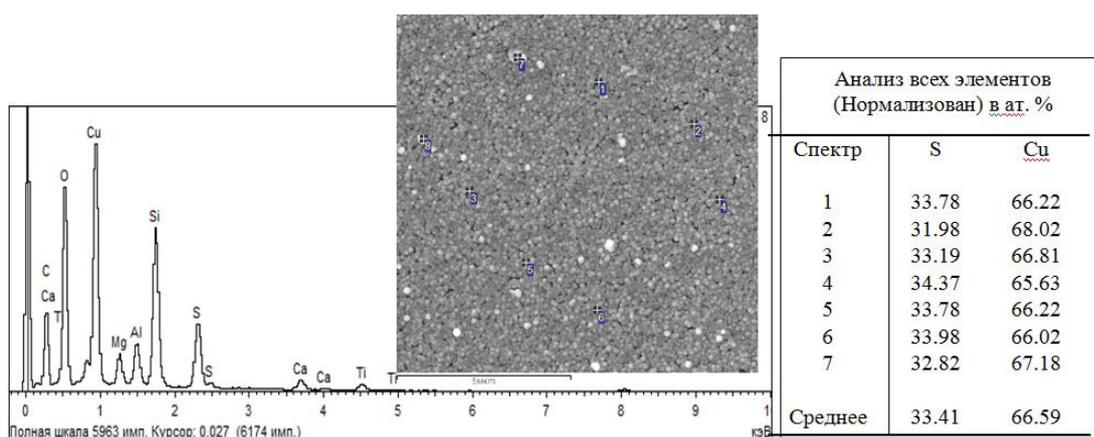
Figures 1-2 show electronic microscopic images of obtained films with the indication of ranges of local element analysis. Its results showed that the separate granules and interphase surface of films from ammoniac system consist of copper and sulfur with the content  $66.59 \pm$  and  $33.41 \pm 1.0$  at. %.



**Fig. 1.** Results of energy-dispersive analysis of  $\text{Cu}_2\text{S}$  film produced by hydrochemical deposition from acetated system at temperature 298 K

For layers from the acetated system these values are  $66.82 \pm 0.58$  and  $33.18 \pm 0.58$  at. % correspondingly. The obtained results show high stoichiometry of synthesized semiconductive layer of  $\text{Cu}_2\text{S}$  in both reaction systems. The presence of bands of oxygen, calcium, titanium, magnesium, aluminium, silicon is determined by the nature of sital substrate consisting of oxides of elements mentioned above.

It should be noted that more homogeneous composition of copper (I) sulfide film was obtained from acetated reaction bath.

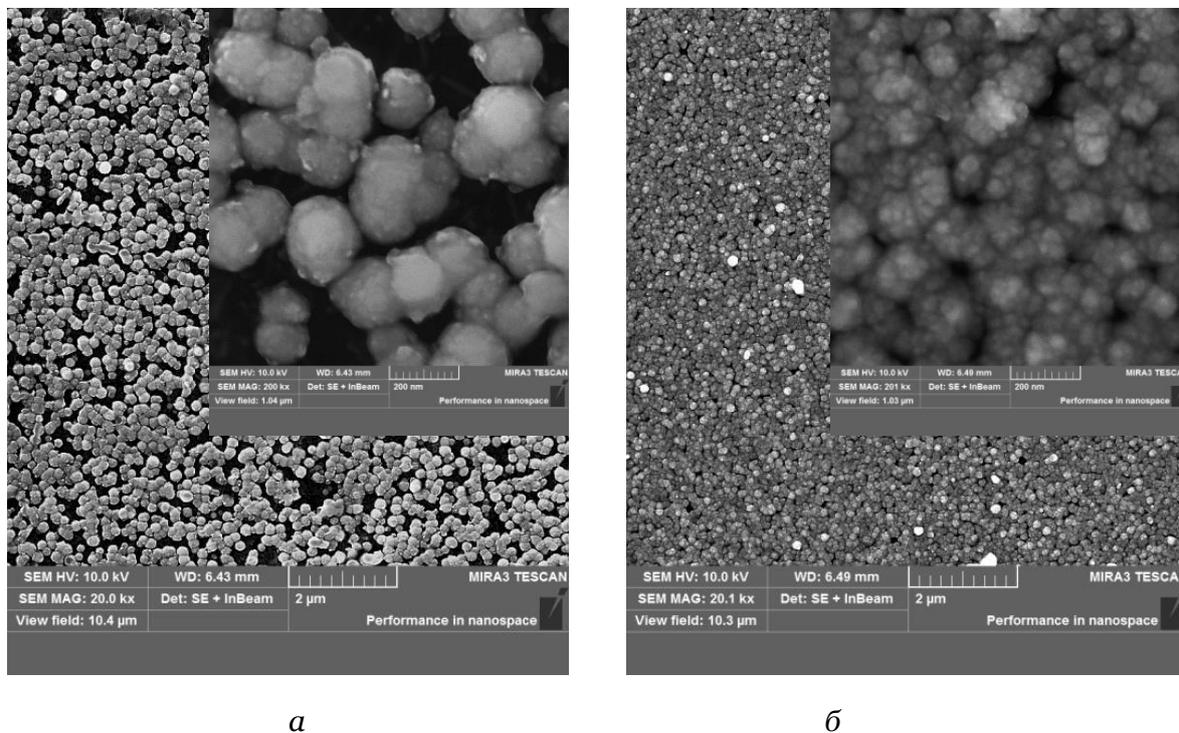


**Fig. 2.** Results of energy-dispersive analysis of  $\text{Cu}_2\text{S}$  film produced by hydrochemical deposition from ammoniac system at temperature 343 K

To study the surface relief of  $\text{Cu}_2\text{S}$  films synthesized in ammoniac and acetated reaction systems raster electron microscopy method was used. Microimages are given on Fig. 3.

Microimages show that the most homogeneous layer of copper sulfide is formed on the sital matrix surface from acetated system. It has a rather dense arrangement. Layers from ammoniac reaction system are distinguished by lower uniformity. It can be explained by the following.

The calculated values of supersaturation show that the formation of copper sulfide film in both systems ammoniac ( $1.59 \times 10^{10}$ ) and acetated ( $1.52 \times 10^8$ ) occurs in high supersaturated solutions. However, it should be considered that the calculation of ionic equilibria was made at 298 K for both systems; whereas hydrochemical synthesis of copper sulfide films in acetated bath was carried out at 343 K. Temperature increasing intensifies synthesis process, increasing the rate of interaction between copper and thiocarbamide with the formation of sulfide solid phase.



**Fig. 3.** Electron-microscopic images of Cu<sub>2</sub>S films deposited at 298 K in the course of 120 min from ammoniac system (a) and at 343 K in the course of 45 min from acetated system (b)

Despite the significant differences in morphology of the layers obtained from studied systems it can be said that independently from the compound of baths spherical globules are the main structure elements that the layers of Cu<sub>2</sub>S are consisted of. These globules are formations of smaller particles preliminarily of spherical shape. Undoubtedly, the size and the shape of structure elements of the film are influenced by deposition process intensity, which is determined by the conditions in reactor, particularly by different temperatures of deposition process. Thus, in acetated system (Fig.3) the formation of copper (I) sulfide film occurs from globules with enough homogeneous size (~10 nm) which attach to each other densely, forming agglomerates with the size up to 80-150 nm. In ammoniac bath where the synthesis was carried out at 298 K larger agglomerates of spherical shape with diameter 180-200 nm are formed.

Electron-microscopic images of Cu<sub>2</sub>S films generally confirmed the signified cluster-cluster mechanism of film growth that was proved by us in research works [23, 24]. It suggests the formation of nuclei of primary clusters of solid phase in the bulk of solution, their growth and subsequent adsorption on the substrate.

One more factor that leads to differences in morphology of deposited layers of Cu<sub>2</sub>S can be the nature influence, particularly structure-spatial parameters of ligands introduced in the system. Thus, ligands possessing branched spatial structure can make difficult the interaction of primary clusters of sulfide phase with growing Cu<sub>2</sub>S film. First, it refers to acetate ions that have two carbon atoms, the first one is connected with three hydrogen atoms, and the second one with two oxygen atoms. Such spatial configuration makes additional difficulties for collisions of primary clusters between each other in the bulk of reaction mixture, with film surface and slows down the rate of film growth. As a result, Cu<sub>2</sub>S layers are produced with more organized and denser surface structure. Ammonium molecule with one central nitrogen atom surrounded by three hydrogen atoms cannot have such a strong blocking influence on aggregation of particles.

## Conclusion

1. Nanocrystal films of copper (I) sulfide with the thickness  $100 \pm 10$  nm exhibiting good adhesion to siall substrate were obtained by hydrochemical deposition in systems « $\text{CuSO}_4 - \text{NaAc} - \text{CS}(\text{NH}_2)_2$ » and « $\text{CuSO}_4 - \text{NH}_3 - \text{CS}(\text{NH}_2)_2$ ». EDX analysis confirmed that at hydrochemical deposition the formation of thin  $\text{Cu}_2\text{S}$  film phase which is closed to stoichiometric composition with the average content of metal and sulfur 66.59 and 33.41 at.%, 66.82 and 33.18 at.% in acetated and ammoniac systems correspondingly occurs.

2. Morphology of obtained films  $\text{Cu}_2\text{S}$  was studied by electron-microscopic research, their nanocrystal nature was determined.

## Aknowledgements

The study was financially supported by the Ministry of Education and Science of the Russian Federation in the framework of the governmental task №4.1270.2014/K.

## References:

1. Burgelman M., Vos A.D. Evaporation of  $\text{CuCl}$  and  $\text{CuCl}_2$  for the fabrication of  $\text{Cu}_x\text{S}/\text{CdS}$  thin film solar cells // *Thin Solid Films*. 1983. Vol.102. P. 367-374.
2. Wang S.Y., Wand W., Lu Z.H. Asynchronous – pulse ultrasonic spray pyrolysis deposition of  $\text{Cu}_x\text{S}$  ( $x = 1, 2$ ) thin films // *Mater. Sci. Eng. B*. 2003. Vol.103. P.184-188.
3. Isac L., Duta A., Kriza A., Manolache S., Nanu M. Copper sulfides obtained by spray pyrolysis – possible absorbers in solid state solar cells // *Thin Solid Films*. 2007. Vol.515. P.5755-5758.
4. He Y.B., Polity A., Osterreicher I., Pfisterer D., Gregor R., Meyer B.K., Hardt M. Hall effect and surface characterization of  $\text{Cu}_2\text{S}$  and  $\text{CuS}$  films deposited by RF sputtering // *Physica B: Condensed Matter*. 2001. Vol.308-310. P. 1069-1073.
5. Santheep K.M., Rajesh N.P., Ichimura M., Ichimura U. Preparation and characterization of copper sulphide particles by photochemical method // *Materials Letters*. 2008. Vol.62. P. 591-593.
6. Ichimura M., Takeuchi K., Nakamura A., Arai E. Photochemical deposition of Se and CdSe films from aqueous solutions // *Thin Solid Films*. 2001. Vol.384. P. 157-159.
7. Sahraei R., Noshadi S., Goudarzi A. Growth of nanocrystalline  $\text{CuS}$  thin films at room temperature by a facile chemical deposition method // *RSC Advances*. 2015. Vol.5. No. 94. P. 77354-77361.
8. Pathan H.M., Desai J.D., Lokhande C.D. Modified chemical deposition and physio-chemical properties of copper sulphide ( $\text{Cu}_2\text{S}$ ) thin films // *Appl. Surf. Sci*. 2002. Vol. 202. P. 47-56.
9. Ramya M., Ganesan S. Influence of thickness and temperature on the properties of  $\text{Cu}_2\text{S}$  thin films // *Iranian J. of Sci. and Tech*. 2013. Vol. 37. No. 3. P. 293-300.
10. M.P. Zhilenko, G.V. Erlih, G.V. Lisichkin. Poluchenie i modifizirovanie poverhnosti nanorazmernogo sul'fida med (Production and surface modification of nanoscaled copper sulfide). *Ross. Nanotech*. 2009. No83. P.5-6.
11. Maskaeva L.N., Shemyakina A.I., Markov V.F., Saryeva R.Kh. Prognozirovanie uslovij himicheskogo osazhdeniya i mikrostruktura nanokristallicheskih plenok sul'fida cinka (Prognostication of chemical deposition conditions and microstructure of nanocrystalline zinc sulphide films) // *J. Applied Chem*. 2015. Vol. 88. No 9. P. 115-125.
12. Markov V.F., Maskaeva L.N., Ivanov P.N. Gidrokhimicheskoe osazhdenie plenok sul'fidov metallov: modelirovanie I eksperiment (Hydrochemical deposition of metal sulfides films: modeling and experiment), Yekaterinburg: Ural. Otd. Ross. Akad. 2006. 218p.
13. Dhanasekar M., Bakiyaraj G., Rammurthi K. Structural, morphological, optical and electrical properties of copper sulphide nanocrystalline thin films prepared by chemical bath deposition method // *Int. J. of Chem. Tech. Res*. 2015. Vol. 7. No. 3. P. 1057-1064.
14. Sateesh P., Madhusudhanarao P. Structural, optical and electrical properties of  $\text{Cu}_2\text{S}$  thin films deposited by CBD method // *Int. J. of Adv. Res. in Phys. Sci*. 2015. Vol. 2. No.11. P. 11-16.
15. Shinde M.S., Patil R.S. Gas sensitivity of  $\text{Cu}_2\text{S}$  thin films by CBD route // *Int. J. of Chem. and Phys. Scie*. 2014. Vol. 3. Spec. Iss. P. 34-43.
16. Shide M.S., Ahirrao P.B., Patil I.J., Disawal S.K., Patil R.S. Studies on physical properties of nanocrystalline  $\text{Cu}_2\text{S}$  thin films prepared modified chemical bath deposition method (M-CBD) //

J. Nanoelectronics and materials. 2013. No.6. P.29-35.

17. Paravee V.-U., Chih-Hung C. Growth Kinetics of Copper Sulfide Thin Films by Chemical Bath Deposition // J. of Solid State Sci. and Tech. 2013. Vol. 2. No.4. P. 120-129.

18. Kassim A., Min H.S., Siang L.K., Nagalingam S. SEM, EDAX and UV-visible studies on the properties of Cu<sub>2</sub>S thin films // Chalcogenide Letters. 2011. Vol.8. No.7. P.405-410

19. Manjulavalli T.E., Kannan A.G. Effects of deposition time on structural, optical and electrical properties of chemically deposited Cu<sub>2</sub>S thin films // J. Chem.Tech. Res. 2015. Vol. 8. No.11. P. 607-616.

20. Krylova V., Dukstienė N., N. Prosyceva N. Deposition and characterization of copper sulphide layers on the home-made polycarbonate plates // Khimija. 2014. Vol. 25. No.3. P. 137-144.

21. Shevcova O.N., Bek R.Yu., Zelinskij A.G., Vajs A.A. Zakonomernosti anodnogo povedeniya zolota v kislyh tiokarbamidnyh rastvorah po dannym ciklicheskoj vol'tamperometrii i kvarcevoj mikrogravimetrii (Laws of the anod behavior of gold in acid thiocarbamide solutions according to cyclic voltammetry and quartz microgravimetry) // Russian J. of Electrochemistry. 2006. Vol. 42. No 3. P. 279-285.

22. Yang X., Moats M.S., Miller J.D. The interaction of thiourea and formamidine disulfide in the dissolution of gold in sulfuric acid solutions // Miner. Eng. 2010. Vol. 23. P. 698-704.

23. Markov V.F., Maskaeva L.N. Osobennosti zarodysheobrazovaniya i mehanizm rosta plenok sul'fidov metallov pri osazhdenii tiokarbamidom (Features of nuclei formation and mechanism of metal sulfide film growth by deposition with thiocarbamide) // Russian Chemical Bulletin. 2014. No 7. P. 1523-1532.

24. Markov V.F., Maskaeva L.N. Osobennosti formirovaniya plenok sul'fidov metallov iz vodnyh rastvorov (Features of the formation of metal sulfide films from aqueous solutions) // Butlerovskie Soobshch. 2011. Vol. 24. No 2. P. 42-50.