

Thematic course: Chemical bath synthesis of metal chalcogenide films. Part 32.

## Influence of the particle size forming polycrystal $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ films on the composition

© Larisa N. Maskaeva,<sup>1,2+</sup> Anastasia D. Kutyavina,<sup>1</sup> Vyacheslav F. Markov,<sup>1,2\*</sup>  
Roman E. Yagovitin,<sup>1</sup> and Irina V. Vaganova<sup>2</sup>

<sup>1</sup>Physical and Colloid Chemistry department. Ural Federal University Named after the First President of Russia B.N. Yeltsin. Mira St., 19. Yekaterinburg, 620002. Sverdlovsk Region. Russia.

Phone: +7 (343) 375-93-18. E-mail: mln@ural.ru

<sup>2</sup>Chemistry and Combustion Process Department. Ural State Fire Service Institute of Emergency Ministry of Russia. Mira St., 22. Yekaterinburg. 620062. Sverdlovsk Region. Russia. Phone: +7 (343) 360-81-68.

\*Supervising author; <sup>+</sup>Corresponding author

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### Abstract

The variability of electro-physical properties of films of solid substitutional  $\text{Cd}_x\text{Pb}_{1-x}\text{S}$  solutions makes them promising as functional materials for optoelectronics, nanoelectronics, sensor engineering, and solar power engineering. Researchers often prefer chemical deposition from aqueous media among all the methods for the production of these films. It is technologically simple and allows obtaining the layers of solid solutions with a high level of supersaturation for CdS substitutional component. A good correlation between the linear sizes of the microcrystallites forming films and the content of the substitutional component in the solid solution was determined at chemical bath synthesis of  $\text{Cd}_x\text{Pb}_{1-x}\text{S}$  films in the ammonium-citrated, ethylenediamine, and ethylenediamine-citrated reaction systems. The range of linear sizes with the minimum diameter of crystallite grains (0.03-0.04  $\mu\text{m}$ ) corresponds to the most enriched solid  $\text{Cd}_x\text{Pb}_{1-x}\text{S}$  solution for CdS component, where  $x = 0.116$  mol. %, deposited in the ammonium-citrated system. In the ethylenediamine-citrated system the maximum of cadmium content in  $\text{Cd}_x\text{Pb}_{1-x}\text{S}$  ( $x = 0.187$ ) corresponds to the particle size 35-40 nm. Two extreme points corresponding to the maximum content of CdS in the solid  $\text{Cd}_x\text{Pb}_{1-x}\text{S}$  solution ( $x = 0.062$  and  $0.089$ ) are observed on the curve of cadmium sulphide content for the ethylenediamine reaction mixture. The values of the substitutional component correspond to the average size of crystallites about 35 nm. Discovered behavior of the dependences “particle size – composition” proves the pronounced size effect while formation of films of supersaturated solid  $\text{Cd}_x\text{Pb}_{1-x}\text{S}$  solutions by chemical deposition. It is connected with the increasing of the contribution of the surface energy of the particles into Gibbs free energy at decreasing their linear sizes. The system realizes its free energy into the formation of highly supersaturated solid solutions. The limits of the mutual solubility of its components broaden even in the ranges of relatively low temperatures of the synthesis.

### References

- [1] M.A. Barote, A.A. Yadav, T.V. Chavan, E.U. Masumdar. Characterization and photoelectrochemical properties of chemical bath deposited  $n$ -PbS thin films. *Digest J. of Nanomaterials and Biostructures*. **2011**. Vol.6. No3. P.979-990.
- [2] M.A. Mohammed, A.M. Mousa, J.P. Ponpon. Optical and optoelectric properties of PbCdS Ternary Thin Films Deposited by CBD. *J. Semicond. Tech. Sci.* **2009**. Vol.9. P.117-123.
- [3] L.E. Shelimova, V.N. Tomashik, V.I. Gricyv. Phase diagrams in semiconducting material science (systems based on Si, Ge, Sn, Pb). *M.: Nauka*. **1991**. 256p. (russian)
- [4] Yu.I. Vesnin. On threshold temperature of the formation of solid substitutional solutions. *Izvestia of SB AS USSR. Series Chem Sc.* **1987**. Vol.17. No.5. P.145-149. (russian)
- [5] Yu.I. Vesnin. On formation mechanism of solid substitutional solutions. *Izvestia of SB AS USSR. Series Chem Sc.* **1985**. Vol.15. No.5. P.7-10. (russian)

- [6] V.F. Markov, L.N. Maskaeva, G.A. Kitaev. Predicting the composition of  $Cd_xPb_{1-x}S$  films deposited from aqueous solutions. *Inorg. Mater.* **2000**. Vol.36. No12. P.1421-1423.  
DOI:10.1023/A:1026613127267
- [7] V.F. Markov, L.N. Maskaeva, J.S. Polikarpova. Films of supersaturated solid solutions of  $Cd_xPb_{1-x}S$  chemically deposited on porous glass, their structure and properties. *Butlerov Communications*. **2006**. Vol.8. No.1. P.54-61. ROI: jbc-02/06-8-1-54
- [8] V.F. Markov, L.N. Maskaeva, P.N. Ivanov. Chemical bath deposition of metal sulfide films: modeling and experiment. *Ekaterinburg: UrO RAN*. **2006**. 218p. (russian)
- [9] A.Yu. Kirsanov, V.F. Markov, L.N. Maskaeva. Solid solution  $Cd_xPb_{1-x}S$  forecasting by simulating of sulfides lead and cadmium co-precipitation process. *Vestnik of South-Ural University. Chemistry*. **2013**. Vol.5. No1. P.35-39.
- [10] E. Pentia, V. Draghici, G. Sarau, B. Mereu, L. Pintilie, F. Sava, M. Popescu. Structural, electrical, and photoelectrical properties of  $Cd_xPb_{1-x}S$  thin films prepared by chemical bath deposition. *Journal of the Electrochemical Society*. **2004**. Vol.151. Iss.11. P.G729-G733.  
DOI:10.1149/1.1800673
- [11] G-L Tan, L. Liu, W. Wu. Mid-IR band gap engineering of  $Cd_xPb_{1-x}S$  nanocrystals by mechanochemical reaction. *AIP Advances*. **2014**. Vol.4. P.067107.  
DOI:10.1063/1.4881878
- [12] K.E. Suryavanshi, R.B. Dhake, A.M. Patil. Optical properties of  $Pb_xCd_{1-x}S$  thin films prepared by chemical bath deposition method. *International J. of Advanced Scientific and Technical Research*. **2014**. Vol.2. Iss.4. P.858-861.
- [13] J.C. Osuwa, C.I. Oriaku, F.I. Ezema. Impurity effects of cadmium salt on the absorption edge and structure of chemically prepared PbS films. *Chalcogenide letters*. **2009**. Vol.6. No.8. P.385-391.
- [14] R. Montenegro, K. Landfester. Metastable and Stable Morphologies during Crystallization of Alkanes in Miniemulsion Droplets. *Langmuir*. **2003**. Vol.19. Iss.15. P.5996-6003.  
DOI:10.1021/la027019v
- [15] C.X. Wang, G.W. Yang. Thermodynamics of metastable phase nucleation at the nanoscale. *Materials Sci. Eng.* **2005**. R.49. Iss.6. P.157.  
DOI:10.1016/j.mser.2005.06.002
- [16] A. Adamson. Physical chemistry of the surface. *M.: Mir*. **1979**. 568p. (russian)
- [17] V.L. Tauson, M.G. Abramovich. Physical-chemical changes of real crystals in mineral systems. *Novosibirsk: Nauka. Siberian Branch*. **1988**. 272p. (russian)
- [18] G.I. Savvakina, V.I. Trefilov. Principle of self-organization in crystallization of metastable phases in strongly nonequilibrium conditions. *Reports of AS USSR*. **1987**. Vol.293. No1. P.91-94. (russian)
- [19] N.F. Uvarov, V.V. Boldyrev. Size effects in chemistry of heterogeneous systems. *Russ. Chem. Reviews*. **2001**. Vol.70. No4. P.265-284.  
DOI:10.1070/RC2001v070n04ABEH000638
- [20] R.F. Khairutdinov. Chemistry of semiconductor nanoparticles. *Russ. Chem. Reviews*. **1998**. Vol.67. No2. P.109-122.  
DOI:10.1070/RC1998v067n02ABEH000339
- [21] V.F. Markov, L.N. Maskaeva. Characteristics of nucleation and mechanism of growth of metal sulfide films at deposition by thiocarbamide. *Izvestia of AS. Series Chem*. **2014**. No7. P.1523-1532 (russian)
- [22] L.N. Maskaeva, E.A. Fedorova, A.I. Shemyakina, E.I. Stepanovskih, V.F. Markov. Kinetic-thermodynamic analysis of the colloid-chemical deposition conditions and AFM-investigation of SnS films. *Butlerov Communications*. **2014**. Vol.37. No.2. P.1-9. ROI: jbc-02/14-37-2-1
- [23] A.S. Katysheva, V.F. Markov, L.N. Maskaeva. Mechanism of  $PbSe_yS_{1-y}$  film formation in chemical deposition from aqueous solutions. *Russ. J. of Inorg. Chem*. **2013**. Vol.58. No7. P.833-838.  
DOI:10.7868/s0044457x1307012x
- [24] A.I. Kitajgorodskij. X-ray structure analysis of fine-crystalline and amorphous materials. *M-L.: State Press House of technical literature*. **1952**. 588p. (russian)