Thematic Section: Physicochemical Research. **Full Paper**
Subsection: Physical Inorganic Chemistry. *Reference Object Identifier* – ROI: jbc-02/17-50-6-95
Publication is available for discussion in the framework of the on-line Internet conference "*Butlerov readings*".
http://butlerov.com/readings/
Submitted on June 17, 2017.

Thematic course: Chemical bath synthesis of metal chalcogenide films. Part 33.

Experimental verification of the ranges of CdS and PbS co-deposition by thiocarbamide in the presence of triethanolamine

© **Larisa N. Maskaeva**,[1,2+] **Vyacheslav F. Markov**,[1,2]*
Anna S. Eremina,[1] and **Irina V. Vaganova**[2]
[1] *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*
[2] *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; +Corresponding author

Keywords: ionic equilibria, triethanolamine, calculation of boundary conditions of chemical deposition, chemical bath deposition, lead sulfide, cadmium sulfide, solid solutions.

Abstract

Ionic equilibria were calculated in the reaction systems for obtaining films of substitutional CdPbS solid solutions by chemical bath co-deposition of lead and cadmium sulfides. Three reaction systems were studied with the following combinations of complexing agents: triethanolamine and ammonia (triethanolamine-ammonium system), triethanolamine and sodium citrate (triethanolamine-citrated system), and triethanolamine and ethylenediamine (triethanolamine-ethylenediamine system). Thiocarbamide was used as a chalcogenizer for sulfide deposition.

Lead and cadmium hydroxyl complexes are the main complexes preventing rapid formation of lead and cadmium sulfides in the triethanolamine-ammonium system in the pH ranges of intense decomposition of thiocarbamide. The contribution of triethanolamine and ammonia to complex formation is negligible at certain ligand concentrations in this system. In the triethanolamine-citrated bath both cadmium and lead exist in the form of hydroxyl-citrated complexes in the solution at pH of sulfide chemical deposition. Lead also forms $Pb(OH)_4^{2-}$ hydroxyl complex. Complexes of cadmium with ethylenediamine are prevailing component in the alkaline ranges in the triethanolamine-ethylenediamine system, whereas lead mainly exists in the form of hydroxyl complexes.

Boundary conditions and ranges of formation of CdS, PbS, $Cd(OH)_2$, $Pb(OH)_2$, $CdCN_2$, $PbCN_2$ were determined to evaluate deposition conditions of major and impurity phases (metal hydroxides and cyanamides) by thermodynamic calculations considering sizes of critical nucleus in the studied reaction systems. The results of calculations are presented as 3D dependences of "initial concentration of metal salt - pH of the solution – concentration of ligand". The reaction mixtures for film chemical deposition were composed based on the calculations and the preliminary experiments. Homogeneous CdPbS layers with thickness 100-300 nm were obtained on sitall substrates for all studied reaction systems at 373 K.

References

[1] S. Kumar, B. Bhattacharya. Variation of band gap in CdPbS with composition prepared by a precipitation technique. *Indian J. of Pure and Appl. Phys*. **2005**. Vol.43. P.609-611.
[2] M.A. Barote, A.A. Yadav, E.U. Masumdar. Effect of deposition parameters on growth and characterization of chemically deposited $Cd_{1-x}Pb_xS$ thin films. *Chalcogenide Lett*. **2011**. Vol.8. No.2. P.129-138.
[3] H.S. Al-Jumaili. Structural and optical properties of nanocrystalline $Pb_{1-x}Cd_xS$ thin films prepared by chemical bath deposition. *Appl. Phys. Research*. **2012**. Vol.4. No.3. P.75-82. DOI:10.5539/apr.v4n3p75

[4] P.L. Nichols, Zh. Liu, L. Yin, S. Turkdogan, F. Fan, C.Z. Ning. $Cd_xPb_{1-x}S$ alloy nanowires and heterostructures with simultaneous emission in mid-infrared and visible wavelengths. *Nano Lett*. **2015**. Vol.15. P.909-916. DOI:10.1021/nl503640x
[5] L. Peña-Cabrera, A. Arizmendi-Morquecho, P. Vorobiev. Thin film CdS/PbS solar cell by low temperature chemical bath deposition and silver doping of the window layer. *J. of Non-Oxide Glasses*. **2016**. Vol.8. No.3. P.59-66.
[6] M. Kamruzzman, R. Dutta, J. Podder. Synthesis and characterization of the as-deposited $Cd_{1-x}Pb_xS$ thin films prepared by spray pyrolysis technique. *Semiconductors*. **2012**. Vol.46. No.7. P.957-961. DOI:10.1134/s1063782612070111
[7] A.S. Obaid, M.A. Mahdi, Z. Hassan, M. Bououdina. Preparation of chemically deposited thin films of CdS/PbS solar cell. *Superlatties and Microstructures*. **2012**. Vol.52. P.816-823. DOI:10.1016/j.spmi.2012.06.024
[8] D.A. Caselli, C.Z. Ning. High-performance laterally-arranged multiple-bandgap solar cells using spatially composition-graded $Cd_{1-x}Pb_xS$ nanowires on a single substrate: a design study. *Opt. Express*. **2011**. Vol.19. P.A686-A694. DOI:10.1364/OE.19.00A686
[9] 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. *J.of the Electrochem. Society*. **2004**. Vol.151. No.11 P.G729-G733. DOI:10.1149/1.1800673
[10] S.R. Deo, A.K. Singh, L. Deshmukh, L.J. Paliwal, R.S. Singh. Studies on structural, morphological and optical behavior of chemically deposited $Cd_{0.5}Pb_{0.5}S$ thin films. *Optik-International J. for Light and Electron Optics*. **2015**. Vol.126. **No.**20. P. 2311-2317. DOI:10.1016/j.ijleo.2015.05.130
[11] L.N. Maskaeva, V.F. Markov, G.A. Kitaev. Synthesis of films of $Cd_{1-x}Pb_xS$ solid solutions by deposition from aqueous media under dynamic conditions. *Russ. J. of Appl. Chem.* **2000**. Vol.73. No5. P.751-753.
[12] 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
[13] 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)
[14] 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.
[15] 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
[16] O.P. Moreno, M.C. Portillo, M.M. Flores, J.M. Juárez, G.A. Ávila, R.L. Morales, O.Z. Ángel. Properties of chemical bath deposited PbS Thin Films Doped with Cd^{2+}. *J. of Materials Science and Engineering A 1*. **2011**. P.759-767.
[17] M.A. Barote, A.A. Yadav, L. P. Deshmukh, E.U. Masumdar. Synthesis and characterization of chemically deposited $Cd_{1-x}Pb_xS$ thin films. *Journal of Non-Oxide Glasses.* **2010**. Vol.2. No.10. P.151-165.
[18] H. Sattarian, T. Tohidi, S.H. Rahmatallahpur. Effect of TEA on characteristics of CdS/PbS thin filmsolar cells prepared by CBD. *Materials Science-Poland*. **2016**. Vol.34. No.3. P.540-547. DOI:10.1515/msp-2016-0072
[19] A.E. Martell, R.D. Hancock. Metall complexes in aqueous solutions. *Plenum Press. N. Y.-London*. **1996**. 253p.
[20] J.N. Butler. Ionic equilibria. *Moscow: Khimia*. **1973**. 448p. (russian)
[21] V.F. Markov, L.N. Maskaeva. Calculating the boundary conditions of the formation of solid-phase metal sulfides and selenides by deposition with thio- and selenourea. *Journal of Physical Chemistry*. **2010**. Vol.86. No8. P.1421-1426. (russian)