Publication is available for discussion in the framework of the on-line Internet conference "*Butlerov readings*".
http://butlerov.com/readings
Submitted on November 17, 2018.

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

Chemicalbathdeposition of *n*-tipe thin films of HgSe by sodium selenosulfate

© **Larisa N. Maskaeva,**[1,2+] **Anastasiya D. Kutyavina,**[1] and **Vyacheslav F. Markov**[1,2]*
[1] *Physical and Colloid Chemistry department. Ural Federal University Named after the First Presidentof Russia B.N. Yeltsin. Mira St., 19. Yekaterinburg, 620002. Sverdlovsk Region. Russia. Phone: +7 (343) 375-93-18. E-mail: mln@ural.ru*
[2] *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 equilibrium, sodium selenosulfate, boundary conditions of formation, chemical bath deposition, thin films, mercury selenide, elemental composition, morphology.

Abstract

Thin films of binary semiconductor compound HgSe are of interest as materials for basic research due to its unusual band structure, as well as for practical use as IR detectors, IR emitters, tunable lasers, ultrasonic and gas sensors, catalysts, reflective materials, transducers of solar energy. Existing methods of producing semiconductor HgSe layers include physical and chemical principles. Itis noted that chemical precipitation of mercury selenide with sodium selenosulfate, which excludes the formation of metal cyanamide, is promising method. Based on the idea of the reversible nature of the hydrolytic decomposition of sodium selenosulfate in aqueous solutions, a thermodynamic analysis of the conditions for the deposition of the mainZnSe and impurity $Zn(OH)_2$ solid phases was carried out in the alkaline systems "$Hg(NO_3)_2 – NH_4SCN – Na_2SeSO_3$" and "$Hg(NO_3)_2 – NH_4SCN – NH_4I – Na_2SeSO_3$" (pH = 8.9), and their boundary conditions of formation were established.The possibility of controlling the process of hydrochemical deposition of a film of mercury selenide, in particular, the preparation of nano-crystalline selenide of mercury by introducing an additional ligand, ammonium iodide, was experimentally shown. An REM study of the HgSe surface morphology revealed that the film from rhodanide reaction mixturea is uniform and dense and has a bimodal distribution of particle size with maxima in the 60-80 nm and 140-160 nm ranges, globules are formed from smaller spherical particles.

There is a trimodal distribution in the rhodanide-iodide reaction system, size of particalsincreace in each maximum. The range is 140-160 nmfor the first maximum, 220-240 nmfor the second, and 300-320 nmfor the third. EDX analysis established the non-stoichiometric content of basic elements (Hg: Se = 50.8; 49.2 at.%).In the HgSe film deposited from the rhodanide reaction mixture the introduction of ammonium iodide NH4I to the mixture leads to a slight decrease in the composition of the mercury film to 50.20 at.%, a decrease in the selenium content to 47.14 at.% and the appearance of iodine in the amount of 2.66 at.%. According to the Hall EMF sign, mercury selenide films has the *n*-type of conductivity.

References

[1] P. Tribolet, J.P. Chatard, A. Manissadjian. Progress in HgCdTe homojunction infrared detectors. *J. Cryst. Growth.* **1998**. Vol.184-185. No.2. P.1262-1271. DOI:10.1016/S0022-0248(98)80263-7
[2] G. Marimuthu, K. Ramalingam, C. Rizzoli, M. Arivanandhan. Solvothermal preparation of nano-b-HgS from a precursor, bis(dibenzyldithiocarbamato) mercury (II). *J. Nanopart. Res*. **2012**. Vol.14. No.2. P.710-720. DOI:10.1007/S11051-011-0710-7
[3] M. Salavati-Niasari, M. Esmaeili-Zare, A. Sobhani. Cubic HgSe nanoparticles: sonochemical synthesis and characterization. *Micro & Nano Letters*. **2012**. Vol.7. No.12. P.1300-1304. DOI:10.1049/mnl.2012.0709
[4] R.S. Patil, C.D. Lokhande, R.S. Mane, S.W. Han. Successive ionic layer adsorption and reaction (SILAR) trend for nanocrystalline mercury sulfide thin films growth. *Mater. Sci. Eng.* **2006**. Vol.B129(1). No.4. P.59-63. DOI:10.1016/j.mseb.2005.12.027

[5] K.A. Higginson, M. Kuno, J. Bonevich, S.B. Qadri, M. Yousuf, H. Mattoussi. Synthesis and characterization of colloidal β-HgS quantum dots. *J. Phys. Chem. B*. **2002**. Vol.106. No.39. P.9982-9985. DOI:10.1021/jp026232x

[6] S.Y. Girgis, A.M. Salem, M.S. Selim. Structural characterization and refractive index dispersion analysis of HgSe thin films grown by reactive solutions. *J. Phys. Condens. Matte.* **2007**. Vol.19. No.11. P.116213-116224. DOI:10.1088/0953-8984/19/11/116213

[7] V. Vankatasamy, N. Jayaraju, S.M. Cox, C. Thambidurai, M. Mathe, J.L. Stickney. Deposition of HgTe by electrochemical atomic layer epitaxy (EC-ALE). *J. Electroanal. Chem*. **2006**. Vol.589. No.2. P.195-202. DOI:10.1016/j.jelechem.2006.02.006

[8] P.P. Hankare, V.M. Bhuse, K.M. Garadkar, A.D. Jadhav. A novel method to grow polycrystalline HgSe thin film. *Mater. Chem. Phys*. **2001**. Vol.71. No.1. P.53-57. DOI:10.1016/S0254-0584(01)00272-3

[9] H. Wang, J.J. Zhu. A sonochemical method for the selective synthesis of alpha-HgS and beta-HgS nanoparticles. *Ultrason. Sonochem*. **2004**. Vol.11. No.5. P.293-300. DOI:10.1016/j.ultsonch.2003.06.002

[10] Y.T. Park, S.G. Lee, Y.U. Kim. Light-induced hydrogen and oxygen generation from water. *Int. J. Hydrogen Energy.* **1995**. Vol.20. No.9. P.711-715. DOI:10.1016/0360-3199(95)00004-W

[11] G. Nimtz, J.X. Huang, J. Lange, L. Mester, H. Spieker. Electron wave interference effects in CMT and quantum-size devices. *Semicond. Sci. Technol*. **1991**. Vol.6. No.12C. P.130-136. DOI:10.1088/0268-1242/6/12C/027

[12] G. Weisbuch, B. Vinte. Quantum semiconductor structures. Fundamental and Applications. *N.Y.: Academic Pres.* **1991**. 252p.

[13] M.J. Kelly. Low-dimensional semiconductors: materials, physics, technology, devices. *Clarendon Press Oxford*. **1995**. 546p.

[14] J.H. Davies. The physics of low-dimensional semiconductors. An Introduction. *Cambridge University Press.* **1998**. 438p. DOI:10.1017/CBO9780511819070

[15] T. Ando, Y. Arakawa, K. Furuya, S. Komiyama, H. Nakashima. Mesoscopic physics and electronics. *Springer Verlag Berlin Heidelberg*. **1998**. 282p.

[16] V.F. Radantsev, A.M. Yafyasov, V.B. Bogevolnov, I.M. Ivankiv, O.Yu. Shevchenko. Zero-field spin splitting in HgTe surface quantum well. *Surface Science.* **2001**. Vol.482-485. No.20. P.989-993. DOI:10.1016/S0039-6028(00)01088-8

[17] M.I. Korsunsky, A.D. Volchek, V.M. Smurygin. New anomalous photoconductors. *Letters to JETP.* **1974**. Vol.20. No.10. P.654-657. (russian)

[18] B.L. Helmondt. The effect of potential nonlocality on the spectrum of holes in semiconductors with a small band gap. *Physics and technology of semiconductors*. **1975**. Vol.9. No.10. P.1912-1914. (russian)

[19] J. Yun, K. Cho, Y. Park, S. Yang, J. Choi, S. Kim. Thermoelectric characteristics of nanocomposites made of HgSe and Ag nanoparticles for flexible thermoelectric devices. ***Nano Research***. **2016**. Vol.10. No.2. P.683-689. DOI:10.1007/s12274-016-1327-z

[20] B. Martinez, C. Livache, A. Robin, H. Cruguel, S. Royer, X.Z. Xu, H. Aubin, S. Ithurria, E. Lhuillier. Intraband transition in self-doped narrow band gap colloidal quantum dots. *Quantum Sensing, Nano Electronics, and Photonics XIV*. **2017**. Vol.10111. P.101112S-101114S. DOI:10.1117/12.2250155

[21] L. Parthier, H. Wissmann, S. Luther, G. Machel, M. Schmidbauer, R. Kohler, M. Von Ortenberg. Growth and characterization of lattice-matched HgSe. *J. Cryst. Growth*. **1997**. Vol.175-176. No.5. P.642-646. DOI:10.1016/S0022-0248(96)00993-1

[22] Y. Lansari, J.W. Cook, J.F. Schetzina. Growth of HgSe and $Hg_{1-x}Cd_xSe$ thin films by molecular beam epitaxy. *J. of Electronics materials.* **1993**. Vol.22. No.8. P.809-812. DOI:10.1007/BF02817490

[23] V. Venkatasamy, M.K. Mathe, S.M. Cox, U. Happek, J.L. Stickney. Optimization studies of HgSe thin film deposition by electrochemical atomic layer epitaxy (EC-ALE). *Electrochim. Acta*. **2006**. Vol.51. No.6. P.4347-4351. DOI:10.1016/j.electacta.2005.12.012

[24] M.E. Martins, R.C. Salvarezz, A.J. Arvia. The electrodeposition of mercury from aqueous Hg_2^{2+} ion-containing acid solutions on smooth and columnar-structured platinum electrodes. *Electrochim. Acta.* **1998**. Vol.43. No.5-6. P.549-561. DOI:10.1016/S0013-4686(97)00129-1

[25] D.R. Salinas, E.O. Cobo, S.G. Garcia, J.B. Bessone. Early stages of mercury electrodeposition on HOPG. *J. Electroanal. Chem*. **1999**. Vol.470. No.2. P.120-125. DOI:10.1016/S0022-0728(99)00220-X

[26] C. Natarajan, M. Sharon, C. Levy-Clement, M. Neumann-Spallart. Electrochemical deposition of n-zinc mercury selenide thin films. *Thin Solid Films.* **1995**. Vol.257. No.1. P.46-53. DOI:10.1016/0040-6090(94)06352-4

[27] G. Mattsson, L. Nyholm, A. Olin. *J.* Cathodic stripping voltammetry of HgSe. *Electroanal. Chem*. **1994**. Vol.377. No.1-2. P.149-162. DOI:10.1016/0022-0728(94)03456-7

[28] C.N. Van Huong, R. Triboulet, P. Lemasson. Ag and Cu deposits on HgXTe (X = Cd, Zn) alloys. *J. Cryst. Growth*. **1990**. Vol.101. No.1-4. P.311-317. DOI:10.1016/0022-0248(90)90988-W

[29] T. Mahalingam, A. Kathalingam, C. Sanjeeviraja, R. Chandramohan, J.P. Chu, Y. DeakKim, S. Velumani. Electrodeposition and characterization of HgSe thin films. *Materials Characterization*. **2007**. Vol.58. No.8-9. P.735-739. DOI:10.1016/j.matchar.2006.11.022
[30] C. Reig, Y.S. Paranchych, V. Munoz-Sanjose. Crystal growth of HgSe by the cold travelling heater method. *Cryst. Growth Des*. **2002**. Vol.2. No.2. P.91-92. DOI:10.1021/cg0155503
[31] Y. Li, Y. Ding, H. Liao, Y. Qian. Room-temperature conversion route to nanocrystalline mercury chalcogenides HgE (E=S,Se,Te). *J. Phys. Chem. Solids.* **1999**. Vol.60. No.7. P.965-968. DOI:10.1016/S0022-3697(98)00349-7
[32] P.P. Hankare, B. Vijaykumar, K.M. Garadkar, I.S. Mulla. Low temperature route to grow polycrystalline cadmium selenide and mercury selenide thin films. *Materials Chemistry and Physics.* **2003**. Vol.82. No.3. P.711-717. DOI:10.1016/S0254-0584(03)00365-1
[33] B. Vijaykumar, P.P. Hankare. Low temperature synthesis of cubic CdSe, HgSe and (CdHg)Se thin films and their characterization. *Ionics*. **2004**. Vol.1. No.3. P.304-310. DOI:10.1007/BF02382836
[34] S.M. Ishiwu, M.N. Nnbuchi. Studies on growth and characterization of mercury selenide thin films prepared by chemical bath technique. *J. of Ovonic Research.* **2011**. Vol.7. No.1. P.9-14. ISSN:18422403
[35] P.P. Hankare, V.M. Bhuse, K.M. Garadkar, S.D. Delekar, I.S. Mulla. Chemical deposition of cubic CdSe and HgSe thin films and their characterization. *Semiconductor Science and Technology*. **2004**. Vol.19. No.1. P.70-75. DOI:10.1088/0268-1242 /19/1/012
[36] V.M. Bhuse, P.P. Hankare. Low temperature synthesis of cubic CdSe, HgSe and (CdHg)Se thin films and their characterization. *Ionics*. **2004**. Vol.10. No.3. P.304-310. DOI:10.1007/BF02382836
[37] V.F. Markov, L.N. Maskaeva, P.N. Ivanov. Chemical bath deposition of metal sulfide films: modeling and experiment. *UrORAN.* **2006**. 218p. (russian)
[38] V.F. Markov, L.N. Maskaeva. Calculation of the boundary conditions for the formation of the solid phase of sulfides and selenides by the deposition of thio- and selenium urea. *Journal of Physical Chemistry*. **2010**. Vol.6. No.8. P.1421-1426. DOI:10.1134/S0036024410080030 (russian)
[39] E.A. Fedorova, L.N. Maskaeva, V.F. Markov, M.V. Kuznetsov, O.A. Lipina, A.V. Pozdin. Copper (I) selenide thin films: composition, morphology, structure, optical properties. *Physics and technology of semiconductors*. **2018**. Vol.52. No.10. P.1213-1219. DOI: 10.21883/FTP.2018.10 (russian)
[40] L.N. Maskaeva, V.F. Markov, E.A. Fedorova, M.V. Kuznetsov. The influence of the conditions of hydrochemical deposition of thin ZnSe films on their morphology and internal mechanical stresses. *Physics and technology of semiconductors*. **2018**. Vol.91. No.9. P.1346-1356. DOI:10.1134/S004446181809013X (russian)
[41] A.A. Timina, L.N. Maskaeva, K.A. Karpov, V.F. Markov. Precursor compounds for Cu_2ZnSe_2 structure. *Sino-Russian ASRTU Conference alternative energy: materials, technologies, and devices, KnE materials science.* **2018**. P.32-38. DOI:10.18502/kms.v4i2.3034.
[42] O.A. Lipina, L.N. Maskaeva, V.F. Markov, E.A. Fedorova, E.A. Klochko. Optical properties of Cu_2S/SnS_2 precursor layers for the preparation of kesterite Cu_2SnS_3 photovoltaic absorber. *Sino-Russian ASRTU conference alternative energy: materials, technologies, and devices. KnE materials science.* **2018**. P.39-44. DOI:10.18502/kms.v4i2.3035
[43] Yu.Yu. Lurie. Handbook of analytical chemistry. *Moscow: Chemistry.* **1971**. 456p. (russian)
[44] G.A. Kitaev, A.Zh. Khvorenkova. Analysis of the conditions for the production of metal selenides in aqueous solutions of sodium selenosulfate. *J. of Appl. Chem.* **1998**. Vol.1. No.8. P.1261-1264. (russian)
[45] J. Choi, K. Cho, J. Yun, Y. Park, S. Yang, S. Kim. Large voltage generation of flexible thermoelectric nanocrystal thin films by finger contact. *Adv. Energy Mater*. **2017**. Vol.21. No.7. P.1700972/1-1700972/7. DOI:10.1002/aenm.201700972