

Thematic course: Chemical bath synthesis of metal chalcogenide films. Part 42.

Experimental verification of the deposition regions of PbSe by sodium selenosulfate and selenourea in the presence of various ligands

© Larisa N. Maskaeva,^{1,2+} Victoria M. Yurk,¹ Anastasia V. Belceva,¹ Ivan V. Zarubin,¹
Anastasia D. Kutuyavina,¹ and Vyacheslav F. Markov^{1,2*}

¹Physical and Colloidal 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

²Chemistry and Combustion Process Department. Ural State Fire Service Institute of Emergency Ministry of Russia. Mira St., 22. Yekaterinburg, 620022. Sverdlovsk Region. Russia. Phone: +7 (343) 360-81-68.

*Supervising author; †Corresponding author

Keywords: ionic equilibria, sodium selenosulfate, selenourea boundary conditions of formation, hydrochemical deposition, thin films, lead selenide.

Abstract

Calculation of ionic equilibria in the reaction system for synthesis of PbSe thin films was carried out. Three reaction systems containing the following combinations of reagents were considered: sodium citrate with liquid ammonia and sodium selenosulfate (system 1) or selenourea (system 2) used as chalcogenizer, ethylenediamine, sodium acetate and selenourea (system 3). The main lead complex compounds prevented the fast PbSe formation in system 1 and 2 in region of pH of intensive selenosulfate and selenourea decomposition were hydroxo-citrate complexes. In the system 3 complexes with ethylenediamine and acetate-ions played the most significant role. For evaluating the deposition conditions of the main and impurity phases (metal hydroxides and cyanamides) by thermodynamic calculations taking into account the sizes of critical nuclei, the boundary conditions and regions of formation of PbSe, Pb(OH)₂, PbCN₂ in the studied reaction systems were found. The calculation results are presented in the form of three-dimensional dependencies in the coordinates “indicator of the initial concentration of the metal salt – pH of the solution – ligand concentration” and “indicator of the initial concentration of the metal salt – pH of the solution – concentration of the chalcogenizer”. Based on the calculations and preliminary experiments, the compositions of the discussed reaction mixtures were formed for the chemical bath deposition of PbSe films, which, in addition to the main components, included a dopant in the form of ammonium iodide. In the synthesis process at a temperature of 353 K (system 1 and 2) for 60 minutes and 308 K for 90 minutes (system 3), using all the studied reaction systems on glass substrates, homogeneous PbSe layers with a thickness of ~500 to ~700 nm were obtained. The ratio between the main elements of Pb and Se in the film varies between 0.98-1.32, and the iodine content is 7-11 at.% depending on the composition of the reaction bath.

References

- [1] J.B. Seung, K. Kim, K.S. Lim, S.M. Jung, Y.-C. Park, D.G. Han, S. Lim, S. Yoo, S. Jeong. Low-temperature annealing for highly conductive lead chalcogenide quantum dot solids. *J. Phys. Chem. C*. **2011**. Vol.115. No.3. P.607-612.
- [2] J. Androulakis, I. Todorov, J. He, D.-Y. Chung, V. Dravid, M. Kanatzidis. Thermoelectrics from abundant chemical elements: high-performance nanostructured PbSe–PbS. *Am. Chem. Soc.* **2011**. Vol.133. P.10920-10927
- [3] S.P. Zimin, E.S. Gorlachev. Nanostructured lead chalcogenides: monograph. *Yaroslavl: Yaroslavl State University*. **2011**. 232p.
- [4] S.P. Zimin, I.I. Amirov, V.V. Naumov. Changes in the Conductivity of Lead-Selenide Thin Films after Plasma Etching. *Semiconductors*. **2016**. Vol.50. No.8. P.1125-1129.
- [5] W. Feng, H. Zhou, F. Chen. Impact of thickness on crystal structure and optical properties for thermally evaporated PbSe thin films. *Vacuum*. **2015**. Vol.114. P.82-85.

- [6] A.D.R. Pillai, K. Zhang, K. Bollenbach, D. Nminibapiel, W. Cao, H. Baumgart, V.S.K. Chakravadhanula, C. Ktibel, V. Kochergin. ALD growth of PbTe and PbSe superlattices for thermoelectric applications. *ECS Trans.* **2013**. Vol.58. No.10. P.131-139.
- [7] D.A. Carder, A. Markwitz, R.J. Reeves, J. Kennedy, F. Fang. Atomic retention and near infrared photoluminescence from PbSe nanocrystals fabricated by sequential ion implantation and electron beam annealing. *Nuclear Instruments and Methods in Physics Research B.* **2013**. Vol.307. P.154-157.
- [8] X. Sun, K. Gao, X. Pang, H. Yang, A.A. Volinsky. Structure and composition effects on electrical and optical properties of sputtered PbSe thin films. *Thin solid films.* **2015**. Vol.592. P.59-68.
- [9] V. Kubát, M. Babiak, Z. Trávníček, J. Novosad. 3-(Diphenylchalcogenophosphoryl)propionic acids as precursors for metal selenides and tellurides. *Polyhedron.* **2017**. Vol.124. P.62-67.
- [10] K.C. Preetha, T.L. Remadevi. Effect of hydrazine hydrate concentration on structural, surface morphological and optoelectronic properties of SILAR deposited PbSe thin films. *Materials Science in Semiconductor Processing.* **2015**. Vol.39. P.178-187.
- [11] B.B. Jin, Y.F. Wang, X.Q. Wang, J.H. Zeng. Pulsed voltage deposited lead selenide thin film as efficient counter electrode for quantum-dot-sensitized solar cells. *Applied Surface Science.* **2016**. Vol.369. P.436-442.
- [12] S. Lin, X. Shi, J. Wei, D. Lu, Y. Zhang, H. Kou, X. Zhang, C. Wang. Nanoscale semiconductor $Pb_{1-x}Sn_xSe$ ($x=0.2$) thin films synthesized by electrochemical atomic layer deposition. *Applied Surface Science.* **2011**. Vol.257. P.5803-5807.
- [13] Y. Suh, S.-H. Suh, S.Y. Lee, G.-H. Kim. Morphological and microstructural evolution of PbSe films grown on thermally oxidized Si (111) substrates by chemical bath deposition. *Thin Solid Films.* **2017**. Vol.628. P.148-157.
- [14] R.B. Kale, S.D. Sartale, V. Ganesan, C.D. Lokhande, Y.-F. Lin, S.-Y. Lu. Room temperature chemical synthesis of lead selenide thin films with preferred orientation. *Applied Surface Science.* **2006**. Vol.253. P.930-936.
- [15] D. Kim, H.S. Kim. Solution-processed fabrication of perfectly (200)-oriented lead selenide thin films. *Materials Letters.* **2018**. Vol.215. P.191-194.
- [16] Y. Liu, M. Gibbs, J. Puthussery, S. Gaik, R. Ihly, H.W. Hillhouse, M. Law. Dependence of carrier mobility on nanocrystal size and ligand length in PbSe nanocrystal solids. *Nano Lett.* **2010**. Vol.10. P.1960-1969.
- [17] J.A. Heredia-Cancino, T. Mendivil-Reynoso, R. Ochoa-Landin, R. Ramírez-Bon, S.J. Castillo. Optical and structural properties of PbSe films obtained by ionic exchange of lead oxyhydroxycarbonate in a selenium-rongalite solution. *Materials Science in Semiconductor Processing.* **2016**. Vol.56. P.90-93.
- [18] A. Khataee, S. Arefi-Oskoui, M. Fathinia, A. Esmaeili, Y. Hanifehpour, S.W. Joo, N. Hamnabard. Synthesis, characterization and photocatalytic properties of Er-doped PbSe nanoparticles as a visible light-activated photocatalyst. *J. of Molecular Catalysis A: Chemical.* **2015**. Vol.398. P.255-267.
- [19] Z.I. Smirnova, V.M. Bakanov, L.N. Maskaeva, V.F. Markov, V.F. Voronin. Effect of an iodine-containing additive on the composition, structure, and morphology of chemically deposited lead selenide films. *Physicsof the Solid State.* **2014**. Vol.56. No.12. P. 2561-2567. (russian)
- [20] Z.I. Smirnova, L.N. Maskaeva, V.F. Markov, V.F. Voronin, M.V. Kuznetsov. Ion-exchange synthesis of $Pb_{1-x}Sn_xSe$ thin film solid solutions from an aqueous solution. *J. of materials science and technology.* **2015**. Vol.31. Iss.1. P.790-797.
- [21] V.M. Yurk, L.N. Maskaeva, V.F. Markov, Z.M. Ibragimova, V.S. Ustyugova, and E.I. Stepanovsky. Hydrochemical synthesis of metal chalcogenides films. Part 27. Influence of iodine-containing addition on composition, morphology and structure of PbSe thin films. *Butlerov Communications.* **2015**. Vol.44. No.10. P.40-44. ROI: jbc-02/15-44-10-40
- [22] V.M. Yurk, L.N. Maskaeva, V.F. Markov, E.V. Maraeva, V.A. Moshnikov, L.B. Matyushkin. Effect of ascorbic acid additions on the mechanism underlying the growth of nanostructured pbse films via hydrochemical deposition. *Inorganic materials.* **2018**. Vol.54. No.3. P. 221-228. (russian)
- [23] S.S. Oluyamo, A.S. Ojo, M.S. Nyagba. Characterization of nanostructured lead selenide (PbSe) thin films for solar device applications. *J. of Applied Physic.* **2015**. Vol.7. No.1. P.10-15.
- [24] V.F. Markov, N.A. Tretyakova, L.N. Maskaeva, V.M. Bakanov, H.N. Mukhamedzyanov. Hydrochemical synthesis, structure, semiconductor properties of films of substitutional $Pb_{1-x}Sn_xSe$ solid solutions. *Thin Solid Films.* **2012**. Vol.520. P.5227-5231.
- [25] N. Ghobadi, E.G. Hatam. Surface studies, structural characterization and quantity determination of PbSe nanocrystals deposited by chemical bath deposition technique. *J. of Crystal Growth.* **2015**. Vol.418. P.111-114.

- Full Paper** _____ L.N. Maskaeva, V.M. Yurk, A.V. Belceva, I.V. Zarubin, A.D. Kut'yavina, and V.F. Markov
- [26] F.G. Hone, F.K. Ampong, T. Abza, I. Nkrumah, M. Paal, R.K. Nkum, F. Boakye. The effect of deposition time on the structural, morphological and optical band gap of lead selenide thin films synthesized by chemical bath deposition method. *Materials Letters*. **2015**. Vol.155. P.58-61.
- [27] S. Anwar, S. Anwar, B.K. Mishra. Effect of bath temperature on PbSe thin films prepared by chemical synthesis. *Materials Science in Semiconductor Processing*. **2015**. Vol.40. P.910-916.
- [28] A. Kassim, H.S. Min, S. Monohorn, S. Nagalingam. Synthesis of PbSe thin film by chemical bath deposition and its characterization using XRD, SEM and UV-VIS spectrophotometer. *MAKARA, SAINS*. **2010**. Vol.14. No.2. P.117-120.
- [29] N. Priyadharsini, S. Vairam, M. Thamilselvan. Structural and optical properties of neodymium doped lead chalcogenide (PbSe) nanoparticles. *Optik*. **2016**. Vol.127. P.5046-5049.
- [30] Z. Hens, D. Vanmaekelbergh. Effect of quantum confinement on the dielectric function of PbSe. *Physical review letters*. **2004**. Vol.92. No.2. P.026908-1-026908-4.
- [31] E. Díaz-Torres, M. Ortega-López, Y. Matsumoto, Y.J. Santoyo-Salazar. Simple synthesis of PbSe nanocrystals and their self-assembly into 2D 'flakes' and 1D 'ribbons' structures. *Materials Research Bulletin*. **2016**. Vol.80. P.96-101.
- [32] W. Lv, X. Wang, Q. Qiu, F. Wang, Z. Luo, W. Weng. Hydrothermal synthesis and characterization of novel PbSe dendritic structures. *J. of Alloys and Compounds*. **2010**. Vol.493. P.358-361.
- [33] M.K. Jana, B. Murali, S.B. Krupanidhi, K. Biswas, C.N.R. Rao. Fabrication of large-area PbSe films at the organic-aqueous interface and their near-infrared photoresponse. *J. Mater. Chem. C*. **2014**. No.2. P.6283-6289.
- [34] T.S. Shyju, S. Anandhi, R. Sivakumar, S.K. Garg, R.G. Anandhi, R. Sivakumar, S.K. Garg, R. Gopalakrishnan. Investigation on structural, optical, morphological and electrical properties of thermally deposited lead selenide (PbSe) nanocrystalline thin films. *J. of Crystal Growth*. **2012**. Vol.353. P.47-54.
- [35] H.K. Sadekar. Optical, structural and surface morphology properties of PbSe Thin film deposited by chemical bath deposition. *Intern. J. of Chemical and Physical Sciences*. **2014**. Vol.3. P.109-113.
- [36] A.E. Martell, R.D. Hancock. Metal complexes in aqueous solutions. *N.Y.-London: Plenum Press*. **1996**. 253p.
- [37] J.N. Butler. Ionic equilibrium. *Moscow: Chemistry*. **1973**. 448p. (russian)
- [38] V.F. Markov, L.N. Maskaeva, P.N. Ivanov. Chemical bath deposition of metal sulfide films: modeling and experiment. *Ural Branch of RAS*. **2006**. 218p. (russian)
- [39] F.V. Pozdin, D.D. Smirnova, L.N. Maskaeva, V.F. Markov and G.L. Rusinov. Hydrochemical synthesis of metal chalcogenides films. Part 41. Hydrochemical deposition of thin films of cadmium selenide by sodium selenosulfate. *Butlerov Communications*. **2019**. Vol.59. No.9. P.29-39. ROI: jbc-02/15-44-10-40