Thematic Section: Research into New Technologies. Subsection: Inorganic Chemistry.

Reference Object Identifier – ROI: jbc-02/18-54-4-119 Publication is available for discussion in the framework of the on-line Internet conference "Butlerov readings". http://butlerov.com/readings/

Submitted on March 17, 2018.

Thematic course: Chemical bath synthesis of metal chalcogenide films. Part 37.

Chemical bath deposition of ZnSe films with sodium selenosulfate

© Anastasia A. Timina,¹ Larisa N. Maskaeva,^{1,2+} Vyacheslav F. Markov,^{1,2}* and Konstantin A. Karpov¹

¹ Physical 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*

² Chemistry 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 equilibriums, boundary conditions for deposition, chemical bath deposition, sodium selenosulfate, thin films, zinc selenide.

Abstract

Zinc selenide is one of the most perspective materials for creating electroluminescent structures and lasers on its base which irradiate from blue to infrared specter range. Among existing methods of obtaining semiconductor ZnSe layers the most perspective is chemical bath deposition method which excludes unnecessity in high temperature heating, use of complex and expensive equipment for creation of deep vacuum. Analysis of ionic equilibriums in the system " $ZnCl_2 - H_2O - Na_3Cit$ " showed that more than 99% of zinc ions in the solution with pH range $0 \le pH \le 9$ exist in the form of complex with citrate-ion ZnCit⁻ and other complex forms of zinc are almost absent. With pH = 10.0-12.5 about 50% of zinc exist in solution in the form of neutral hydroxo complex $Zn(OH)_2$. Concentration of $Zn(OH)_4^{2-}$ complex in solution prevails with pH > 13. Thermodynamic estimation of boundary conditions of zinc selenide solid phase formation in the reaction system " $ZnCl_2 - Na_3C_6H_5O_7 - NH_2OH \cdot HCl - NaOH - Na_2SeSO_3$ " allowed to conclude that with pH = 10-12.5 the formation of Zn(OH)₂ solid phase on sitall substrate is possible. This new surface acts as nucleation center for ZnSe solid phase condensation. Due to it, experimental check of possibility to depose zinc selenide with sodium selenosulfate was carried out in neutral range of pH = 6-7. As a result of carried out experiment of chemical bath deposition from the presented reaction mixture zinc selenide films of orange color and having good adhesion to sitall substrate were obtained. Thickness of deposed films reached 800 nm in dependence on deposition conditions. Energy-dispersive elemental analysis established content of main elements in layers, which was on the average for Zn (51.64±1.0 at. %) and Se (48.36±1.0 at. %). It says about lack of halogen in layers in comparison with formula composition. Possibly, it is related with zinc oxygencontaining phase formation $Zn(OH)_2$, which can be predicted in calculation. Shown, that freshly deposed zinc selenide layers have *p*-type conductivity which was established by thermoelectric power sign.

References

- [1] A.N. Georgobiani, M.K. Scheinkman. Physics of A^{II}B^{VI} compounds. *Moscow: Nauka.* **1986**. 320p. (russian)
- [2] V.Ya. Degoda, A.A. Sofienko. Features of zinc selenide luminescence and conductivity while photo- and X-ray excitated. Physics and technic of semiconductors. 2010. Vol.44. No.5. P.594-599. (russian)
- [3] D.D. Nedeoglo, A.V. Simashkevich. Electric and luminescence properties of zinc selenide. Kishinev: publishing house "ShTIITsA". 1984. 150p.
- [4] N.K. Morozova, V.A. Kuznetsov, V.D. Rizhikov. Zinc selenide. Obtaining and optical properties. Moscow: Nauka. 1992. 78p. (russian)
- [5] L.V. Atroshenko, S.F. Burachas, L.P. Galchinetski, B.V. Grinev, V.D. Rizhikov, N.G. Starzhinsky. Crystals of scintillators and detectors of ionizing radiations on its base. Kiev. Naukovadumka. 1998. 312p.
- [6] V.K. Komar', V.M. Puzikov. Single crystals of A^2B^6 group. Growing, properties, application. Kharkiv: Institut monokristallov. 2002. 244p.

Full Paper

- [7] S. Kasap, P. Capper. The Springer Handbook of Electronic and Photonic Materials. Nonlinear Optoelectronic Materials. 2007. 1063p.
- [8] R.G. Valeev, P.N. Krilov, E.A. Romanov. Structure and properties of ZnSe nanocomposite filmes. Surface, X-ray, synchrotron and neutron studies, 2007. No.1. P.41-45. (russian)
- [9] Kh.A. Toshkhodzhaev, S.N. Karimov. Analysis of current transfer processes in heterostructure of disordered zinc selenide base. RAS of Republic of Tajikistan. 2008. Vol.51. No.7. P.507-513.
- [10] S.P. Suprun, V.N. Sherstyakova, E.V. Fedosenko. Epitaxy of ZnSe on GaAs with using ZnSe compound as a source. *Physics and technic of semiconductors*. 2009. Vol.43. No.11. P.1570-1575. (russian)
- [11] R.R. Savfutvarov, A.V. Khomvakov, E.N. Mozhevitina, I.Kh. Avetisov. Nanosized films of cadmium and zinc selenides with controlled nonstoichiometry. Successes in chemistry and chemical technology. 2014. Vol.28. No.6. P.28-30. (russian)
- [12] D.S. Sofronov, V.V. Starikov, T.V. Novikova, E.A. Vaksler, P.V. Mateychenko, A.M. Lebedinski, Ya.A. Bondarenko, D.A. Gaman. Structure and properties of ZnSe films obtained by electrochemical deposition method. Inorganic materials. 2016. Vol.52. No.12. P.1279-1283. (russian)
- S. Oueslati, G. Brammertz, S. Oueslati et. al. Physical and electrical characterization of high-[13] performance Cu₂ZnSnSe₄ based thin film solar cells. *Thin Solid Films*. 2015. Vol.582. P.224-228.
- [14] R. Kondrotas, R. Juškėnas, R. Kondrotas et. al. Characterization of Cu₂ZnSnSe₄ solar cells prepared from electrochemically co-deposited Cu-Zn-Sn alloy. Solar Energy Materials & Solar Cells. 2015. Vol.132. P.21-28. (russian)
- [15] V.F. Markov, L.N. Maskaeva, P.N. Ivanov. Chemical bath deposition of metal sulfides films: modelling and experiment: UB RAS. 2006. 218p. (russian)
- V.F. Markov, L.N. Maskaeva. Calculation of border conditions of sulfides and selenides solid phase [16] formation by deposition with thio- and selenourea. Journal of physical chemistry. 2010. Vol.86. No.8. P.1421-1426. (russian)
- [17] J.N. Butler. Ion equilibria. *Moscow: Khimiya*. 1973. 448p.
- [18] Yu.Yu. Lurie. Handbook of Analytical Chemistry. *Moscow: Khimiya*. **1989**. 448p.