

Thematic course: Hydrochemical synthesis of metal chalcogenide films. Part 27.

Kinetic study of chemical deposition of silver sulphide by thiocarbamide

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Key words: hydrochemical deposition, thiocarbamide, kinetic study, silver sulphide, formal kinetic equation, activation energy of chemical reaction.

Abstract

The article considers kinetic study of chemical deposition of silver sulphide by thiocarbamide form solutions containing silver nitrate, ammonium hydroxide and sodium citrate at temperatures 303-343 K during spontaneous formation of solid phase. Specific kinetic orders are defined in all components of reaction mixture and activation energy of this process is 37 kJ/mole. In the specified concentration limits formal kinetic equation is derived for the rate of conversion of silver salt into silver sulphide that allows providing aimed regulation of the rate of silver sulphide phase formation in the investigated reaction mixture.

References

- [1] H. Meherzi-Maghraoui, M. Dachraoui, S. Belgacem, K.D. Buhre, R. Kunst, P. Cowache, D. Lincot. Structural, optical and transport properties of Ag₂S films deposited chemically from aqueous solution. *Thin Solid Films*. **1996**. Vol.288. Iss.1-2. P.217-223.
- [2] T.B. Nasrallah, H. Dlala, M. Amlouk, S. Belgacem, J.C. Bernede. Some physical investigations on Ag₂S thin films prepared by sequential thermal evaporation. *Synthetic Materials*. **2005**. Vol.151. Iss.3. P.225-230.
- [3] D. Karashanova, D. Nihtianova, K. Starbova, N. Starbov. Crystalline structure and phase composition of epitaxially grown Ag₂S thin films. *Solid State Ionics*. **2004**. Vol.171. Iss.3-4. P.269-275.
- [4] M.M. El-Nahass, A.A.M. Farag, E.M. Ibrahim, S. Abd-El-Rahman. Structural, optical and electrical properties of thermally evaporated Ag₂S thin films. *Vacuum*. **2004**. Vol.72. Iss.4. P.453-460.
- [5] V.B. Prabhune, N.S. Shinde, V.J. Fulari. Studies on electrodeposited silver sulphide thin films by double exposure holographic interferometry. *Appl. Surf. Sci*. **2008**. Vol.255. Iss.5. P.1819-1823.
- [6] V.F. Markov, T.V. Vinogradova, I.V. Zarubin, L.N. Maskaeva. Thin film chemical sensors based on Ag_xPb_{1-x}S_{1-δ} for determination of NO₂ NO and CO content in air. *Analytics and Controls*. **2012**. Vol.16. No4. P.410-414. (russian)
- [7] N.N. Umarova, N.I. Movchan, R.A. YUsupov and others. Diffusion coefficient calculation at ionic exchange of Pb(II)/Ag(I) on thin-film sorbent PbS. *Russ. J. of Physical Chemistry*. **2000**. Vol.74. No.9. P.1707-1709. (russian)
- [8] V.F. Markov, L.N. Maskaeva. Swmiconductive sensitive element of nitrogen oxide gas-analyzer based on lead sulfide. *J. of Analytical Chemistry*. **2001**. Vol.56. No.8. P.546-550. (russian)
- [9] N.N. Umarova, N.I. Movchan, R.A. YUsupov, V.F. Sopin. The influence of complexing agents on ionic exchange of Ag(I)/ Pb(II) in thin polycrystalline films of PbS. *Russ. J. of Physical Chemistry*. **2002**. Vol.76. No.8. P.1485-1488. (russian)
- [10] L.N. Maskaeva, V.F. Markov, T. V. Vinogradova and others. Hydrochemical synthesis and properties of supersaturating solid solutions of substitution of Ag_xPb_{1-x}S_{1-δ}. *The Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*. **2003**. No.9. P.35-42. (russian)

- [11] D. Karashanova, K. Starbova, N. Starbov. Microstructure correlated properties of obliquely vacuum deposited Ag₂S thin films. *J. Optoelectronics & Adv. Mater.* **2003**. Vol.5. No.4. P.903-906.
- [12] E. Korashy, M.A. Abdel-Rahim, H.E. Zahed. Optical absorption studies on AgInSe₂ and AgInTe₂ thin films. *Thin Solid Films*. **1999**. Vol.338. Iss.1-2. P.207-212.
- [13] I.C. Lekshmi, G. Berera, Y. Afsar, G.X. Miao, T. Nagahama, T. Santos, J. Moodera. Controlled synthesis and characterization of Ag₂S films with varied microstructures and its role as asymmetric barrier layer in trilayer junctions with dissimilar electrodes. *J. Appl. Phys.* **2008**. Vol.103. P.093719.
- [14] H. Nozaki, M. Onoda, K. Yukino, K. Kurashima, K. Kosuda, H. Maki, S. Hishita. Epitaxial growth of Ag₂S films on MgO(001). *J. Sol. State Chem.* **2004**. Vol.177. Iss.4-5. P.1165-1172.
- [15] M. Chen, Y. Xie, H.Y. Chen, Z.P. Qiao, Y.T. Qian, Preparation and Characterization of Metal Sulfides in Ethylenediamine under Ambient Conditions through a γ -Irradiation Route. *J. of Colloid Interf. Sci.* **2001**. Vol.237. Iss.1. P.47-53.
- [16] Ali Muhammad, Hamid K., Asif Ali T., Huang Nay M., Wijayantha K.G. Upul, Muhammad M. Synthesis and characterization of silver diethyldithiocarbamate cluster for the deposition of acanthite (Ag₂S) thin films for photoelectrochemical applications. *Thin Solid Films*. **2013**. Vol.536. P.124-129.
- [17] E. Barrera-Calva, M. Ortega-López, A. Avila-García, Y. Matsumoto-Kwabara. Optical properties of silver sulphide thin films formed on evaporated Ag by a simple sulphurization method. *Thin Solid Films*. **2010**. Vol.518. P.1835-1838.
- [18] P.E. Agbo, P.A. Nwofe. Structural and Optical Properties of Sulphurised Ag₂S Thin Films. *Int. J. Thin. Fil.* **2015**. Vol.4. No.1. P.9-12.
- [19] H.M. Pathan, P.V. Salunkhe, B.R. Sankapal, C.D. Lokhande. Photoelectrochemical investigation of Ag₂S thin films deposited by SILAR method. *Materials Chemistry & Physics*. **2001**. Vol.72. Iss.1. P.105-108.
- [20] T. Auttasit, W. Kun-Lun, T. Hao-Yu, L. Ming-Way, W. Gou Jen. Ag₂S quantum dot-sensitized solar cells. *Electrochem. Commun.* **2010**. Vol.12. Iss.9. P.1158-1160.
- [21] S.S. Dhume, C.D. Lokhande. Preparation and characterization of chemically deposited Ag₂S films. *Solar Energy Materials & Solar Cells*. **1992**. Vol.28. Iss.1. P.159-166.
- [22] A. Núñez Rodríguez, M.T.S. Nair, P.K. Nair. Structural, optical and electrical properties of chemically deposited silver sulfide thin films. *Semicond. Sci. Technol.* **2005**. Vol.20. No.6. P.576-585.
- [23] U.M. Jadhav, S.R. Gosavi, S.N. Patel, R.S. Patil. Studies on Characterization of Nanocrystalline Silver Sulphide Thin Films Deposited by Chemical Bath Deposition (CBD) and Successive Ionic Layer. *Arch. Phys. Res.* **2011**. Vol.2. No.2. P.27-35.
- [24] N.A. Forostyanaya, L.N. Maskaeva, V.F. Markov. The influence of ligand nature on the boundary conditions of formation and morphology of nanocrystalline films of CdS. *J. of General Chemistry*. **2015**. Vol.85. No10. P.1596-1601. (russian)
- [25] L.N. Maskaeva, A.I. Shemyakina, V.F. Markova, R.Kh. Saryeva. Prognostication of chemical deposition conditions and microstructure of nanocrystalline zinc sulphide films. *J. Applied Chem.* **2015**. Vol.88. No.9. P.115-125. (russian)
- [26] E.A. Fedorova, L.N. Maskaeva, V.F. Markov, A.N. Ermakov, R.F. Samigulina. Hydrochemical synthesis and thermal stability of nanocrystalline films and residues of copper(I) selenide. *J. of Inorganic Chemistry*. **2015**. Vol.60. No11. P.1432-1438. (russian)
- [27] S.S. Tulenin, V.F. Markov, L.N. Maskaeva. The influence of thermal annealing on structure and composition of nanostructured indium(III) sulfide. *Non-ferrous Metals*. **2015**. No.4. P.28-32. (russian)
- [28] Z.I. Smirnova, V.M. Bakanov, L.N. Maskaeva, V.F. Markov, V.I. Voronin. The influence of iodine addition on composition, structure and morphology of chemically deposited films of lead selenides. *Physics of the Solid States*. **2014**. Vol.56. Iss.12. P.2468-2474. (russian)
- [29] V.F. Markov, T.A. Alekseeva, L.N. Maskaeva. Features of hydrochemical deposition of metal sulfides and selenides films. *Butlerov Communications*. **2015**. Vol.41. No.1. P.8-21. ROI: jbc-02/15-41-1-8
- [30] V.F. Markov, L.N. Maskaeva, M.YU. Porkhachev, O.A. Mokrousova. Thermal and radioactive stability of IR-detectors based on solid solution films of Cd_xPb_{1-x}S. *Fire and Explosion Safety*. **2015**. Vol.24. No9. P.67-73. (russian)
- [31] H.N. Mukhamedzyanov, L.N. Maskaeva, V.F. Markov. Comparative photovoltaic characteristics of nanostructured Pb_{1-x}Sn_xSe films obtained by co-deposition and by layer-by-layer deposition of PbSe and SnSe. *Semiconductors*. **2014**. Vol.48. No2. P.278-282. (russian)
- [32] A.S. Sergeeva, V.F. Markov, L.N. Maskaeva. Thermal sensitisation of chemically deposited films based on solid solutions of PbSe_xS_{1-x}. *Glass Physics and Chemistry*. **2014**. Vol.40. No.2. P.298-307.

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- [33] L.N. Maskaeva, V.F. Markov, V.I. Voronin, A.I. Gusev. Hydrochemical synthesis, structure and properties of films of supersaturated substitutional $\text{Cu}_x\text{Pb}_{1-x}\text{S}$ solid solutions. *Thin Solid Films*. **2004**. Vol.461. P.325-335. (russian)
- [34] S.S. Tulenin, V.F. Markov, L.N. Maskaeva, M.V. Kuznetsov. Hydrochemical deposition and study of thin films in the system $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3$. *Butlerov Communications*. **2013**. Vol.33. No.1. P.97-103. ROI: jbc-02/13-33-1-97
- [35] G. Sharlo. Methods of analytical chemistry. Quantitative analysis of inorganic compounds. *Moscow, Leningrad: Chemistry*. **1965**. 976p. (russian)
- [36] L. Mejtis. Introduction to the course of chemical equilibrium and kinetics. *Moscow: Mir*. **1984**. 484p. (russian)
- [37] D.G. Knorre, L.F. Krylov, V.S. Muzykantov. Physical chemistry. *Moscow: Vysshaya Shkola*. **1990**. 416p. (russian)
- [38] I.V. Pyatnitskij, V.V. Sukhan. Analytical chemistry of silver. *Moscow: Nauka*. **1975**. 264p. (russian)

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Тематическое направление: Гидрохимический синтез пленок халькогенидов металлов. Часть 27.

Кинетические исследования процесса химического осаждения сульфида серебра тиокарбамидом

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Ключевые слова: гидрохимическое осаждение, тиокарбамид, кинетические исследования, сульфид серебра, формально-кинетическое уравнение, энергия активации химической реакции.

Аннотация

Исследована кинетика химического осаждения сульфида серебра тиокарбамидом из растворов, содержащих нитрат серебра, гидроксид аммония и цитрат натрия, при температурах 303-343 К в условиях самопроизвольного зарождения твердой фазы. Определены частные кинетические порядки по всем компонентам реакционной смеси и энергия активации процесса, составившая 37.0 кДж/моль. В заданных концентрационных пределах выведено формально-кинетическое уравнение скорости превращения соли серебра в Ag_2S , позволяющее обеспечить целенаправленное регулирование скорости формирования фазы сульфида серебра в исследуемой реакционной системе.