

Thematic section: Hydrochemical synthesis of the metal chalcogenides thin. Part 35.

Hydrochemical deposition Cu₂S films by sodium thiosulfate

© Larisa N. Maskaeva,^{1,2+} Irina A. Berg,¹ Vyacheslav F. Markov,^{1,2*} and Nikolay V. Berg¹

¹ Department of Physical and Colloidal Chemistry. Ural Federal University of the Name of the First President of Russia B.N. Yeltsin. Mira St., 19. Ekaterinburg, 620002. Sverdlovsk Region. Russia.

Phone: +7 (343) 375-93-18. E-mail: mln@ural.ru

² Ural Institute GPS of the Ministry of Emergency Measures of Russia. Mira St., 22. Ekaterinburg, 620022. Russia. Phone: +7 (343) 360-81-68.

*Supervising author; +Corresponding author

Keywords: copper sulfide(I), thin films, hydrochemical deposition, ionic balance, boundary formation conditions, elemental composition, morphology, conductivity type.

Abstract

Copper sulfide(I) thin films find general application in Solar Cell, as sensitive detectors, switches and thermistors, having optimal values of width of the forbidden zone equal 1.2-1.8 eV. It is noted, that chemical bath deposition have significant perspective, because having a simple hardware design, allows to deposit thin films to dielectric surfaces of different configuration at temperatures below 100 °C. The analysis of publication indicates the domination of the prescription approach to the chemical deposition of copper sulfide(I) thin films by sodium thiosulfate. In this work, a calculation method of estimating the formation of solid phases of metal sulphides and selenides, developed earlier and tested on a large number of metal chalcogenides, was used. The boundary conditions for the formation of copper sulfide(I) were determined at a temperature of 298 K in the reaction system “CuCl₂ – NH₂OH·HCl – C₄H₆O₆ – Na₂SeSO₃” with sodium thiosulfate like chalcogenizer. It is shown that the most preferable for chemical deposition of copper sulfide(I) is the acidic area (pH = 3-4). At the same time, the deposition conditions accompanying the formation of the sulfide, the impurity phase of copper hydroxide CuOH, were found. The use of sodium thiosulfate as a chalcogenizer, as well as the introduction of hydroxylamine hydrochloride, provides the creation of reducing environ with the conversion bivalent copper in monovalent condition and the formation of Cu₂S. With considering selected concentrations of the components of the reaction composition and pH in the considered system, through hydrochemical deposition have been synthesized polycrystalline layers of copper sulfate(I) of dark brown color, up to 200 nm in thickness which have good adhesion to a sittal substrate. Scanning electron microscopy established that the thin-film layer is formed from «petals» with size of 150-200 nm. The elements composition is established by the method of energy dispersive analysis. The deposited layers are characterized by a high stehiometry of the formula composition, and base on the results of thermo EMF method, they have a hole conductivity type.

References

- [1] B. Bharathi, S. Thanikaikarasan, K. Ramesh. Structural, compositional, and optical properties of electrochemically deposited Cu₂S thin films. *International Journal of ChemTech Research*. **2014**. Vol.6. No.3. P.1907-1909.
- [2] H. Sunil, M.P. Chaki, Deshpande, Jiten P. Tailor. Characterization of CuS nanocrystalline thin films synthesized by chemical bath deposition and dip coating techniques. *Thin Solid Film*. **2014**. Vol.6. No.550. P.291-297.
- [3] V.V. Gorbachev. Semiconductor compounds AIBVI. *Moscow: Metallurgy*. **1980**. P.132. (russian)
- [4] L. Isac, A. Duta, A. Kriza, S. Manolache, M. Nanu. Copper sulfides obtained by spray pyrolysis - possible absorbers in solid-state solar cells. *Thin Solid Films*. **2007**. Vol.7. No.515. P.5755-5758.
- [5] I.P. Parkin. Solid state metathesis reaction for metal borides, silicides, pnictides and chalcogenides: ionic or elemental pathways. *Chem. Soc. Rev*. **1996**. No.25. P.199-207.
- [6] M. Ramya, S. Ganesan. Influence of thickness and temperature on the properties of Cu₂S thin films. *Iranian J. of Mater. Sci. Eng*. **2011**. No.8. P.34-40.

- [7] Shimao Wang, Weiwei Dong, Xiaodong Fang, Shu Zhou, Jingzhen Shao, Zanhong Deng, Ruhua Tao, Qingli Zhang, Linhua Hu and Jun Zhu. Enhanced electrocatalytic activity of vacuum thermal evaporated Cu_xS counter electrode for quantum dot-sensitized solar cells. *Electrochimica Acta*. **2015**. No.154. P.47-53.
- [8] Gopinath Mondal, Sumanta Jana, Ananyakumari Santra, Moumita Acharjya, Pradip Bera, Dipankar Chattopadhyay, Anup Mondal and Pulakesh Bera. Single-source mediated facile electrosynthesis of p- Cu_2S thin films on TCO ($\text{SnO}_2:\text{F}$) with enhanced photocatalytic activities. *RSC Adv*. **2015**. No.5. P.52235-52242.
- [9] R.T. Srinivasa, R. Amiruddin, M.C. Santhosh Kumar. Deposition and characterization of Cu_2SnS_3 thin films by co-evaporation for photovoltaic application. *Solar Energy Materials and Solar Cells*. **2015**. Vol.143. P.128-134.
- [10] Y. Lu, X. Meng, G. Yi, J. Jia. In situ growth of CuS thin films on functionalized self-assembled monolayers using chemical bath deposition. *J. of Colloid and Interface Sci*. **2011**. Vol.356. Iss.2. P.726-733.
- [11] M. Dhanasekar, G. Bakiyaraj, K. Rammurthi. Structural, Morphological, Optical and Electrical Properties of Copper Sulphide Nano crystalline thin films prepared by chemical bath deposition method. *International Journal of ChemTech Research*. **2015**. Vol.7. No 3. P.1057-1064.
- [12] P. Sateesh, P. Madhusudhanarao. Structural, Optical and Electrical Properties of Cu_2S Thin Films Deposited by CBD Method. *International J. of Advanced Research in Physical Science*. **2015**. Vol.2. No.11. P.11-16.
- [13] M.S. Shinde, R.S. Patil. Gas Sensitivity of Cu_2S Thin Films by CBD Route. *International Journal of Chemical and Physical Sciences. Spec.Iss*. **2014**. Vol.3. P.34-43.
- [14] M.S. Shide, P.B. Ahirrao, I.J. Patil and et.al. Studies on physical properties of nanocrystalline Cu_2S thin films prepared modified chemical bath deposition method (M-CBD). *J. Nanoelectronics and materials*. **2013**. No.6. P.29-35.
- [15] T.E. Manjulavalli, A.G. Kannan. Effects of deposition time on structural, optical and electrical properties of chemically deposited Cu_2S thin films. *J. ChemTech Res*. **2015**. Vol.8. No.11.P.607-616.
- [16] Paravee Vas-Ummuay, Chih-hung Chang Deposition. Growth Kinetics of Copper Sulfide Thin Films by Chemical Bath Deposition. *J. of Solid State Science and Technology*. **2013**. Vol.2. No.4. P.120-129.
- [17] V. Krylova, N. Dukštienė, I. Prosyčeva. Deposition and characterization of copper sulphide layers on the home-made polycarbonate plates. *Chemija*. **2014**. Vol.25. No.3. P.137-144.
- [18] A. Kassim, H.S. Min, L.K. Siang. SEM, EDAX and UV-visible studies on the properties of Cu_2S thin films. *Chalcogenide Letters*. **2011**. Vol.8. No.7. P.405-410.
- [19] Yu.Yu. Lurie. Handbook of analytical chemistry. Moscow: Chemistry. **1989**. 448p. (russian)
- [20] G.A. Kitaev, A.A. Uritskaya, N.S. Belova. Analysis of the formation of metal sulfides in aqueous solutions of sodium thiosulfate. *Journal of Applied Chemistry*. **2000**. Vol.73. No.9. P.1433-1436. (russian)
- [21] S.V. Ryabtsev, A.Yu. Zavrazhnov, S.S. Berezin et al. Obtaining and characterization of Cu_2S film samples. *Condensed matter and interphase boundaries*. **2016**. Vol.18. No.4. P.545-549. (russian)
- [22] P. Sateesh, P. Madhusudhanarao. Structural, Optical and Electrical Properties of Cu_2S Thin Films Deposited by CBD Method. *Intern. J. of Adv. Res. in Phys. Sci*. **2015**. Vol.2. Iss.11. P.11-16.
- [23] I. Grozdanov, M. Najdoski. Optical and electrical properties of copper sulfide films of variable composition. *J. solid state chem*. **1995**. Vol.114. Iss.2. P.469-475.
- [24] M. Ramya, S. Ganesan. Study of electrical transport properties in thermally evaporated Cu_2S thin films. *J. of Applied. Sci. and Eng*. **2012**. Vol.15. No.8.4. P.423-432.