UDC 544.72.05

ZnS Films: Thermodynamic Justification of Possibility for Hydrochemical Precipitation, Synthesis, Microstructure, and Morphology

[1] Anna I. Shemyakina
[2] Ragneta Kh. Saryeva
[3] Larisa N. Maskaeva
[4] Vyacheslav F. Markov

[1] Ural Federal University named after the first President of Russia B.N. Yeltsin, Ekaterinburg, Russian Federation
620002, Ekaterinburg, Mira Street, 19
Assistant researcher
E-mail: anutan145@mail.ru
[2] Ural Federal University named after the first President of Russia B.N. Yeltsin, Ekaterinburg, Russian Federation
620002, Ekaterinburg, Mira Street, 19
Assistant researcher
E-mail: ragneta@rambler.ru
[3] Ural Federal University named after the first President of Russia B.N. Yeltsin, Ekaterinburg, Russian Federation
620002, Ekaterinburg, Mira Street, 19
D. Sc. (Chemical), Professor
E-mail: mln@ural.ru
[4] Ural Federal University named after the first President of Russia B.N. Yeltsin, Ekaterinburg, Russian Federation
620002, Ekaterinburg, Mira Street, 19
D. Sc. (Chemical), Professor, head of the department of physical and colloidal chemistry
E-mail: v.f.markov@ustu.ru

Abstract

The analysis of the thermodynamic equlibria in the «$Zn^{2+} - NH_3 - OH^-$» systems has been carried out; boundary conditions and formations area for ZnS and associated impurity phases of $Zn(OH)_2$ и $ZnCN_2$ have been determined. The nanocrystalline films of zinc sulfide with a thickness of 200-240 nm have been synthesized. The X-ray diffraction analysis and scanning electron microscopy in conjunction with energy-dispersion analysis have been applied for attestation of the structural condition for the zinc sulfide thin films. The effect of the zinc salt nature on the morphology, composition, and structure of the synthesized ZnS layers has been established.

Keywords: ion equilibrium, thermodynamic calculation, chemical precipitation, thin films, zinc sulfide, cubic structure.

Introduction

Zinc sulfide - a binary nontoxic semiconductor of $A^{II}B^{VI}$ group with fine passing capacity in the large interval of wavelengths, low coefficient of reflection, high chemical resistance and thermal stability attracts increased attention of researchers. At 300 K the hexagonal zinc sulfide has the band gap width of 3.74 eV, but the cubic one – 3.66 eV [1]. For the obtained ZnS thin films, which are met and the values of band gap are less: 3.53 eV [2], 3.51 eV [3]. But in any case the band gap width of ZnS is greater than of CdS (E_g = 2.42 eV), which allows to use zinc sulfide as the optical windows for film photocells on the base of $CuInSe_2$ (CIS), $CuIn_{1−x}Ga_xSe_2$ (CIGS) and CdTe compounds. Zinc sulfide can be recommended and both as a potential candidate for cadmium sulfide replacement of CdTe/CdS and CdS/CIGS in heterojunction solar cells. Zinc sulfide has an advantage in delivery of high-energy photons into absorbing material and decreases their intermediate loss to improve the triggering current in the solar cells. Having such properties, ZnS is widely used for the production of various optical devices and is of interest not only as individual material but as one of the components of cascade photocells [4-6].

For the creation of optoelectronic devices of different types thin films are of great interest. Effectiveness of their work is determined by the film properties depending on the way of their preparation. Zinc sulfide obtaining is carried out by the methods of thermal discrete evaporation of the powder ultrahigh vacuum equipment [7], vacuum sublimation in quasi-closed volume [8], electrodeposition [9], and deposiition from gas phase [10], aerosol pyrolysis of aqueous solutions of thiourea coordinating zinc compositions [11]. These methods require large energy expenditures to synthesize zinc sulfide at high temperature and pressures. The hydrochemical method is a perspective method for obtaining zinc sulfide thin films [12]. The method of chemical deposition of metal salts and thiourea [13-16] from aqueous solutions distinguishes from other ones by their essential advantages. It is simple from technical point of view economical and gives good replicated results, as well as allows obtaining $A^{II}B^{VI}$ compounds both as powders and as thin films. The reaction mixtures containing zinc sulfate, chloride and zinc acetate as the complex agents often use ammonia, sometimes sodium citrate are used in published materials on the chemical deposiition from aqueous conditions, thiocarbamide acts as chalcogenizator [17-20]. However scientifically based approach to the determination of optimal conditions for zinc sulfide obtaining which is perspective semiconductor material in thin-film state is absent in these papers.

Therefore the aim of the given work is the thermodynamic value of formation possibility of zinc sulfide films by hydrochemical deposiition, study of morphology, composition and structure of ZnS films.

Experimental

Hydrochemical deposition of zinc sulfide films has been carried out on previously defatted polished glass-ceramic and glass plants made of reaction mixture containing zinc sulfate ($ZnSO_4$), zinc chloride ($ZnCl_2$), thiocarbamide (CSN_2H_4) and ammonium hydroxide (NH_4OH). The film synthesis was carried out in the temperature interval of 348 − 368 K during 120 min in hermetic reactors made of molybdenum glass into which these films were put fixed in specially produced fluoroplastic holders. The reactors were put into thermostat TS − TB − 10 brand supplying accuracy of ±0,1° temperature maintaining.

The thickness of deposited layers was evaluated with interference microscope (Linnik microinterferometer) of MII-4M. Morphology of film surface was studied by scanning electron microscopy (SEM) of MIRA3LMV with increasing from 500 to 150000 times at accelerating voltage of electron beam of 10 or 20 kV. Besides this scanning electron microscope of JEOL JSM-5900 LV equipped with EDS Inca Energy 250 X-ray spectrometer − for energy-dispersive analysis (EDX) − with which surface morphology and the element composition of different parts of the film were studied at accelerating voltage of 10 kV electron beam. The accuracy of the element composition determination was ~10 rel. %.

The XRD patterns were obtained using the standard industrial diffractometer of DRON − 4 with Cu anode and a pyrolytic graphite monochromator separating the $CuK\alpha_{1,2}$ doublet from the continuous spectrum in the range of 2θ from 15 to 100°C scanned at a step of $\Delta(2\theta) = 0.02°$ and a data accumulation time of 5 s per point.

Results and discussions

The chemical reaction of obtaining zinc sulfide films by hydrochemical synthesis can be presented as following:

$$ZnL_x^{2+} + N_2H_4CS + 4OH^- = ZnS\downarrow + xL + CN_2^{2-} + 4H_2O. \tag{1}$$
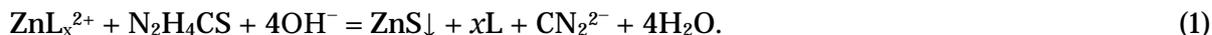
It is necessary for creation and formation of metal sulfide to slow down the process of chemical deposition of this phase by preliminary connection of the metal in the complex. Therefore complex agents different in power and concentration are introduced into reaction mixture.

We developed and tested for the number of reaction systems [12, 21-24] the methodology for determination of boundary conditions and concentration area of solid phase deposition of metal sulfide depending on the pH value and ligand concentration. It is based on the analysis of ion equilibriums in the reaction system and the reversible character of chalcogenizator decomposition [12, 25-27]. At that, the dependence of minimal metal salt composition corresponding to the beginning of the process of it transformation into sulfide on pH value of the reaction mixture is implied as boundary deposition conditions.

Boundary conditions of solid phase deposition in the diluted solutions are realized when ionic product (IP) of ZnS equals to solubility product (SP) of chalcogenide metal. Thus, it is necessary to carry out the following conditions for the formation of the slightly soluble zinc sulfide on the reaction (1):

$$IP_{ZnS} = SP_{ZnS}, \tag{2}$$

where IP_{ZnS} — an ionic product, i.e. the product of noncomplex Zn^{2+} metal form and S^{2-} sulfide ions activities, SP_{ZnS} — the solubility product of ZnS solid phase being of constant value at the given temperature.

However the initiation of some supersaturating value of ZnS appearing in IP_{ZnS}/SP_{ZnS} ratio for compensation of excess surface energy of forming of nuclei and the following growth of new phase particles is necessary for the stable formation of solid phase by homogeneous mechanism.

The value created in the system of supersaturating depends on the concentration of Zn^{2+} free ions in the volume of the reaction mixture.

The higher is supersaturation, the smaller is the Gibbs energy of nuclei formation and the less are nuclei sizes which are able to further growth. The concentration of zinc free ions in the reactor volume is determined by the nature of ligands, which are in the reactor. Deposition of ZnS films from the citrate and ammonia reactions systems containing accordingly $C_6H_5O_7^{3-}$ complexing zinc citrate ions, and NH_3 ammonia was carried out for the evaluation of role and influence of complexing zinc ammonia (NH_3).

The portion of Zn^{2+} noncomplex (active) ions in the presence of ammonia NH_3, which are able to react with sulfide ions can be evaluated according to the expression suggested in [28]:

$$\alpha_{Zn^{2+}} = \frac{[Zn^{2+}]}{C_{Zn}} = \frac{1}{1 + \dfrac{[L_1]}{k_1} + \dfrac{[L_1]^2}{k_{1,2}} + \dots \dfrac{[L_1]^n}{k_{1,2\dots n}}}, \tag{3}$$

where C_{Zn} — the total analytical concentration zinc ions in the solution; L — the concentration of free ligand; k_1, k_2 — instability constants of different complex metal forms.

The following values of the instability constants of complex zinc ions were used in calculations: $pk_4 = 2.18$, $pk_5 = 4.43$, $pk_6 = 6.93$, $pk_7 = 9.08$, $pk_8 = 9.46$, $pk_9 = 12.75$ for complexes with ammonia $ZnNH_3^{2+}$, $Zn(NH_3)_2^{2+}$, $Zn(NH_3)_3^{2+}$, $Zn(NH_3)_4^{2+}$, $Zn(NH_3)_5^{2+}$, $Zn(NH_3)_6^{2+}$ [29]; $pk_{10} = 6.04$, $pk_{11} = 11.1$, $pk_{12} = 13.6$, $pk_{13} = 14.6$ [29] for hydrocomplexes according to $Zn(OH)^+$, $Zn(OH)_2$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$.

In order to determine predominating of complex forms in the solution, which influence jestingly on the rate of deposition process the analysis of ionic equilibria in the «$Zn^{2+} - NH_3 - OH^-$» system, was performed.

The distribution diagram of different complex zinc forms in the aqueous solution in the ammonia system beginning from pH value is shown in Fig. 1.
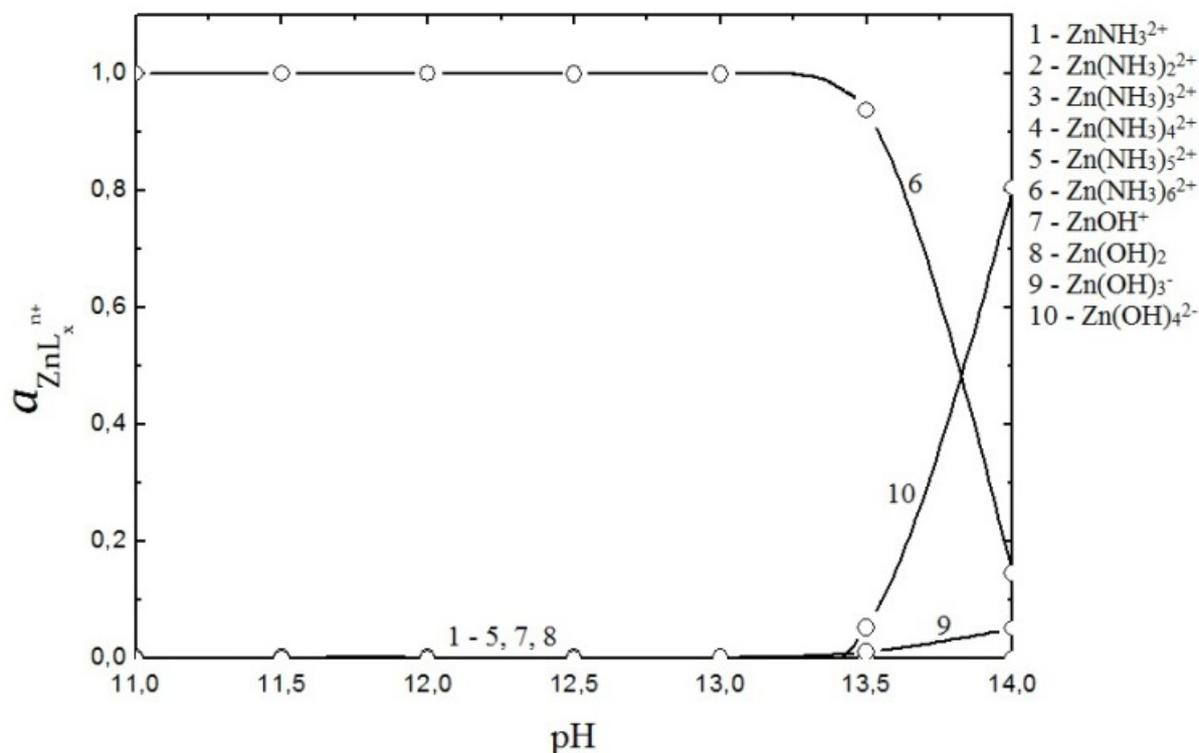
Fig. 1. The diagrams of the distribution of complex zinc forms in the «$Zn^{2+} - NH_3 - OH^-$» system. The initial concentration of zinc salt equals 0.1 mol/l.

The results of ionic equilibria calculations showed that a part of zinc hydrocomplexes in using as ammonia ligands isn`t significant: for $pH < 13.0$ a part is ~0.01. Let us note, that the $Zn(OH)_4^{-2}$ complex ion reaching 0.8, predominants in pH = 14 range. $Zn(NH_3)_6^{2+}$ is the predominant complex preventing the fast zinc sulfide precipitation in the system, when (pH = 10–13) thiocarbamide value is favorable for decomposition (Fig. 1).

The calculation of boundary formation conditions on the base of analysis of ionic equilibria was made, in order to determine, the concentration area of zinc sulfide existence as well as accompanying impurity phases as zinc hydroxide $Zn(OH)_2$ and zinc cyan amide $ZnNH_2$ in the studied system.

Equation [12] was used for the determination of minimally necessary concentrations of zinc salt supporting the ZnS solid phase formation in the investigated reaction system in ammonia presence:

$$pC_H = p\Pi P_{ZnS} - p\alpha_{Zn^{2+}} - \left(pk_{H_2S} - 2pH + 0.5pK_c + p[N_2H_4CS]_H + 0.5p\frac{\beta_\text{п}}{\beta_S} \right) - - \frac{0.86 \cdot \sigma \cdot V_M}{R \cdot T \cdot r_{\text{кр}}}, \quad (4)$$

where p – the index (negative logarithm); C_H – the minimal concentration of zinc salt necessary for ZnS solid phase formation; SP_{ZnS} – the solubility product of zinc sulfide; $\alpha_{Zn^{2+}}$ - part concentration of metal free ions able to enter chemical reaction; k_{H2S} – constant of hydrogen sulfide ionization which is one of thiocarbamide decomposition products (pk_{H_2S} = 19.88 [29]); K_C - constant of thiocarbamide hydrolytic decomposition (pK_c = 22.48 [12]); $[N_2H_4CS]_H$ – initial concentration of chalcogenizator (thiocarbamide) in the solution, 0.6 mol/l; σ – specific surface energy of zinc sulfide (1.0 Дж/м²); V_M – the molar volume of zinc sulfide (2.28·10⁻⁵ м³/моль); $r_{\text{кр}}$ –

radius of critical size nucleus ($3.2 \cdot 10^{-9}$ м); R – universal gas constant 8.314 Дж/(моль·К); T – process temperature (353 K).

The last component in the formula is the derivative from Thomson – Oswald relation and determines supersaturating investment in the ZnS system with the formation of critical size nuclei.

The minimal initial concentration of $pC_{\text{н}}$ zinc salt providing the formation of zinc hydroxide and was obtained by [12]:

$$pC_{\text{н}} = p\Pi P_{Zn(OH)_2} - p\alpha_{Zn^{2+}} - 2pK_W + 2pH_{\text{н}} ,\qquad(5)$$

where $p\Pi P_{Zn(OH)_2}$ - index of solubility product of zinc hydroxide (17.15 [29]); K_W – ionic product of water.

The equation [13] was used for calculation of the boundary conditions formation of zinc cyan amide:

$$pC_{\text{н}} = p\Pi P_{ZnCN_2} - p\alpha_{Zn^{2+}} - \left(pk_{H_2CN_2}^{1,2} - 2pH_{\text{н}} + 0.5pK_C + 0.5p[N_2H_4CS]_{\text{н}} + 0.5p\frac{\beta_S}{\beta_{\text{ц}}}\right),\qquad(6)$$

where $p\Pi P_{ZnCN_2}$ – index of solubility product of zinc cyan amide (14.1 [13]); $k_{H_2CN_2}^{1,2}$ – the total constant of zinc cyan amide decomposition by two stages ($pk_{H_2CN_2}^{1,2} = 21.52$ [13]).

The results of calculations of the boundary conditions and the deposition area of zinc sulfide and zinc hydroxide for this reaction mixture in the form of the three-dimensional graphical dependences in the coordinates of "index of initial concentration of metal salt – concentration introduced ligand – pH values of the solution" are represented in Fig. 2. From results mentioned above is clear that the ZnS solid phase in the ammonia system (Fig. 2) can be formed in pH range from 12 to 14. The value of zinc minimal concentration necessary for proceeding of sulfide formation process grows with increasing of ligand concentration introduced in the reaction mixture.

As it is well known, the formation of films on the non activated substrate is only formation area of the thermodynamically stable metal hydroxide, i.e. the $Zn(OH)_2$ phase is performs a role of natural surface activator, but OH^- ions act as centers of concentration. It is seen in Fig. 2 that the hydroxide phase in presence of which influences positively the initial stage of sulfide formation is formed at pH value higher than 12.
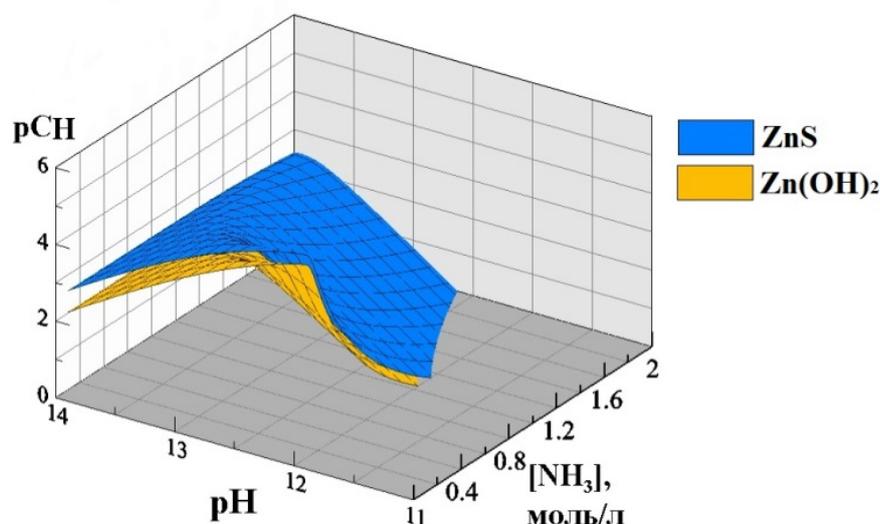
Fig. 2. The boundary conditions of zinc sulfide and hydroxide formation
in the «$Zn^{2+} - NH_3 - N_2H_4CS - OH^-$» system

Calculations have shown that the formation of zinc cyan amide phase in the reaction mixture does not create the necessary conditions.

According to the calculations most favorable for film deposition in the mixture ZnS pH range is from 12 to 14. In this case, the higher the alkalinity of the solution, the lower the required minimum concentration of zinc salt in solution. For films of zinc sulfide in the system studied was selected region pH ~ 12) at a total concentration of the reaction mixture was introduced into the zinc salt 0.1 mol / l.

In terms of the Thomson - Ostwald equation [21] the value of the critical nucleus is directly related to the degree of supersaturating. The calculated value of supersaturating generated in the reaction mixture, when used as ligands of ammonia was 9.9.104, i.e. zinc sulfide film formation should occur under conditions of sufficiently high supersaturating. Due to the large supersaturating it can be assumed that the system will produce a large number of nuclei and the crystal grains of small size.

As a result, the substrate can form a dense and homogeneous film on the structure ZnS.

The results of preliminary experiments and calculations during the two-hour chemical synthesis, conducted at a temperature of 363 K were obtained smooth shiny zinc sulfide layer uniformly covering the surface pyroceramics and glass substrates with good adhesion. Their thickness depending on the conditions of synthesis ranged from 200 to 240 nm.

The SEM images of zinc sulfide layers obtained hydrochemical deposition from a reaction mixture comprising zinc chloride and sulfate are presented in Fig. 3.

a *б*
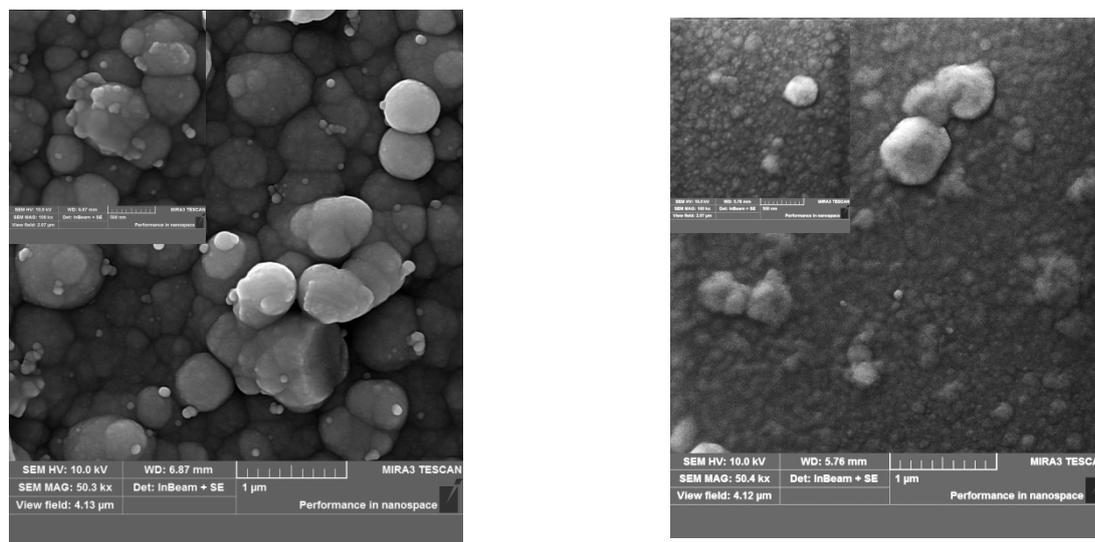
Fig. 3. The SEM images of ZnS films obtained hydrochemical deposition during 120 minutes on the pyroceramics substrates from the reaction mixture, containing zinc chloride (a) and sulfate (b). The temperature of synthesis was 368 K.

Despite their significant differences can be noted that the major structural elements of films regardless of the type of zinc salt in the reaction mixture are preferably spherical globules representing aggregate smaller particles typical spherically shaped zinc sulfide [30]. We see that in both cases a spherical shape with a primary particle size of 10-30 nm form giant clusters of globular shape. However, their diameter and morphology depending on the reaction system is noticeably different. Thus, when using zinc chloride predominant sizes of globules 400-700 nm. More dense and homogeneous film is obtained from a reaction mixture containing zinc sulfate. However, the surface can be observed a minor amount of large aggregates of 200-500 nm in size.

The proximity film of zinc sulfide to the stoichiometric composition is an important criterion for the quality of the optical material is provided that, as stated in [31], while the low-temperature synthesis. In addition, the most perfect crystal structure of the film is synthesized in highly non equilibrium conditions. It meets these requirements hydrochemical deposition used in this paper. But an important factor in the stoichiometric composition of the investigated sulfide has a zinc salt.

The obtained results allows us to conclude that for ZnS approximate to the stoichiometric composition, it is preferable to use zinc chloride, provides the relation between the Zn: S as a 49.3: 50.7 in at. 52.7% vs. 47.3 obtained when in the reactor zinc sulfate.

The XRD patterns of ZnS films (Fig. 5) indicating a preferred crystallographic grain orientation in the [111] direction in the films grown using a reaction mixture of zinc chloride and ammonia as complex agent. Observed on the XRD patterns of investigated sample the intensities of reflection indicates the preferential crystal orientation in the (111) plane. The strong reflex of cubic phase ZnS indicates that it is dominant in the test samples of the films, i.e. synthesized layers of zinc sulfide have a cubic modification of sphalerite with lattice constant $a = 0.5318$ nm. In this work [32] reported that the crystals with [111] orientation are preferable from the viewpoint of optical properties.
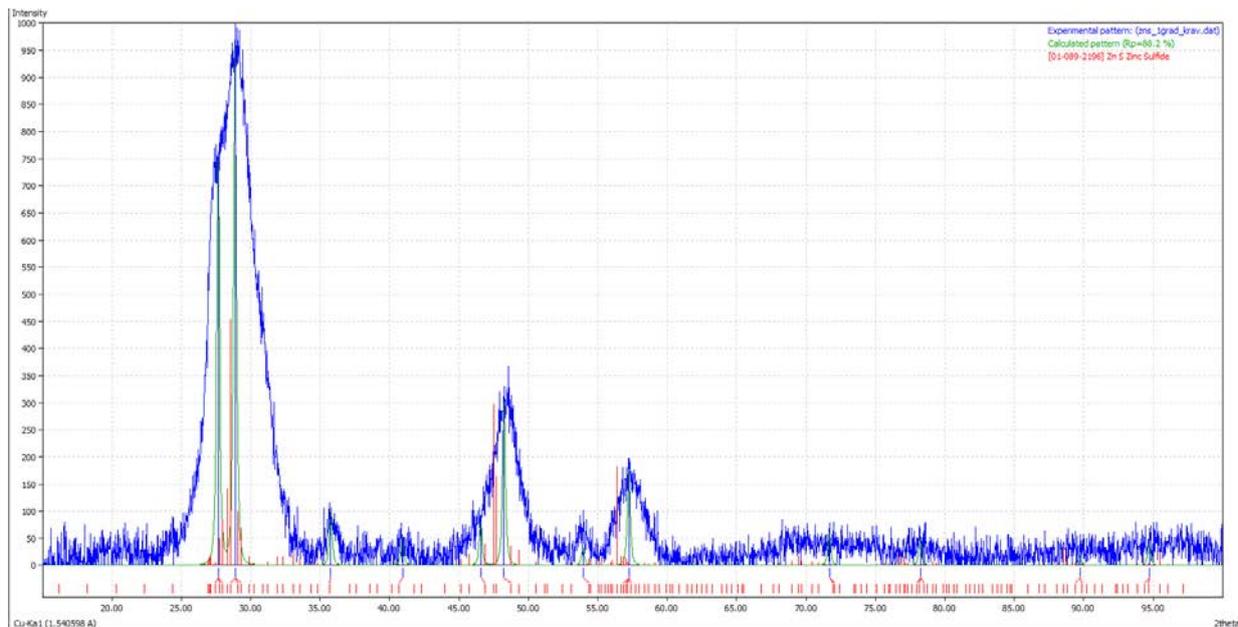
Fig. 4. The XRD pattern of ZnS film obtained by chemical deposition on during 120 minutes on the pyroceramics substrate in presence ammonia mixture, which is zinc chloride. The temperature of synthesis was 368 K.

Despite the complexity of physical and chemical process of synthesis of zinc sulfide films by chemical vapor deposition from aqueous solutions, in the present study because of thermodynamic calculations of ionic equilibria in the «Zn^{2+} - NH_3-N_2H_4CS - OH^-» layers were obtained ZnS, close to the stoichiometric composition of the cubic structure, is an important quality criterion for optical semiconductor material, particularly solar cells and the new film heterostructures.

Acknowledgments

References:

1. Georgobiani A.N., Wide-gap semiconductors $A^{II}B^{VI}$ and prospects of their application // Uspekhi Fizicheskikh Nauk. 1974. Vol. 113. № 1. P. 129–155 [in Russian].

2. Jie Cheng, Dong Bo Fan, Hao Wang, Bing Wei Liu, Yong Cai Zhang, Hui Yan. Chemical bath deposition of crystalline ZnS thin films // *Semicond. Sci. Technol.* 2003. Vol. 18. № 7. P. 676-679.

3. Liu Qi. Guobing Mao, JianpingAo. Chemical bath-deposited ZnS thin films: Preparation and characterization // Applied Surface Science. 2008. Vol. 254. Iss. 18. P. 5711–5714.

4. Chopra K.L, Das S.R. Thin film solar cells. - Plenum Press: New York, London, 1983. 283 p.

5. Dharmadasa I.M. Advances in thin film solar cells. - Pan Stanford Publishing. 2012. 225 p.

6. Kashani H. Production and evaluation of ZnS thin films by the MOCVD technique as alpha-particle detectors // Thin Solid Films. 1996. Vol. 288. Iss.1-2. P. 50-56.

7. Vetoshkin V.M., Krylov P.N., Romanov E.N. Investigation of effect of modes for ion-plazma processing on roughness of supporters made of quartz, polycore, and sytall // Vacuum technics and technology. 2008. V. 18. № 2. P. 75-80.

8. Kurbatov D.I. Electrophysical properties of zinc sulfide films obtained by close-spaced vacuum sublimation technique // Semiconductors. 2013. Vol. 47 (9). P. 1175-1180 [in Russian].

9. Urazov K.A. Dergacheva M.B. Leontyeva K.A. Khussurova G.M. Yaskevich V.I. Electrochemical deposition of zinc sulfide films // Journal chemistry and chemical technology. 2014. №3. P. 36-43 [in Russian].

10. Gavrishchuk E.M., Yashina E.V. Zinc sulfide and zinc selenide optical elements for IR engineering // Journal of Optical Technology. 2004. Vol. 71. № 12. P. 24-31 [in Russian].

11. Klyeva V.G., Mayorova T.L., Fam Thi Hai M., Semenov V.N. Recombination properties of zinc sulfide films, obtained by diffusion technique // Condensed media and interphase boundaries. 2009. Vol. 9. № 2. P. 152-155 [in Russian].

12. Markov V.F., Maskaeva L.N., Ivanov P.N. Hydrochemical precipitation of sulfide metals films: modeling and experiment. - Yekaterinburg, UrO RAS. 2006. 218 p [in Russian].

13. Sorokin E., Naumov S., Sorokina I.T. Ultrabroadband infrared solid-state lasers // IEEE J Sel Top Quant Electron. 2005. Vol. 11. № 3. P. 690-712.

14. Park S., Kim H., Jin C., Lee C. Synthesis, structure, and photoluminescence properties of ZnSSe alloy nanorods // Current Appl. Phys. 2012. V. 12. Iss. 2. P. 499-503.

15. Dharmadasa I.M. Advances in thin film solar cells. - Pan Stanford Publishing. Hardback. 2012. 225 p.

16. Kashani H. Production and evaluation of ZnS thin films by the MOCVD technique as alpha-particle detectors // Thin Solid Films. 1996. V. 288. Iss. 1-2. P. 50-56.

17. Liu Qi, Guobing Mao, Jianping Ao. Chemical bath-deposited ZnS thin films: Preparation and characterization // Applied Surface Science. 2008. Vol. 254. Iss. 18. P. 5711–5714.

18. Jie Cheng, DongBoFan, Hao Wang, BingWei Liu, YongCai Zhang, Hui Yan. Chemical bath deposition of crystalline ZnS thin films // *Semicond. Sci. Technol.* 2003. Vol. 18. № 7. P. 676

19. Ben Nasr T., Kamoun N., Kanzari M., Bennaceur R. Effect of pH on the properties of ZnS thin films grown by chemical bath deposition // Thin Solid Films. 2006. Vol. 500. P. 4–8.

20. Huda Abdullah, Norhabibi Saadah and Sahbuddin Shaari Effect of Deposition Time on ZnS Thin Films Properties by Chemical Bath Deposition (CBD) Technique // World Applied Sciences Journal. 2012. Vol. 19. № 8. P. 1087-1091.

21. Mironov M.P., Loshkareva L.D., Maskaeva L.N., Markov V.F. Kynetics- thermodynamic investigation of tin precipitation (II) in trilonate system by selenourea // Butlerov communications. 2010. V. 19. № 1. P. 25-31 [in Russian].

22. Tulenin S.S., Markov V.F., Maskaeva L.N. Thermodynamic analysis of conditions for formation and chemical precipitation of solid solutions substitution in the $Cu_2S–In_2S_3$ system // Butlerov communications. 2012. Vol. 29. № 3. P. 79-85 [in Russian].

23. Fedorova E.A., Maskaeva L.N., Markov V.F. $Cu_{2−x}Se$ films: thermodynamic analysis of formation conditions, synthesis, composition, morphology // Butlerov communications. 2014. V. 38. № 6. P. 81-87 [in Russian].

24. Maskaeva L.N., Markov V.F., Voronin V.I., Gusev A.I. Hydrochemical synthesis, structure and properties of films of supersaturated substitutional $Cu_xPb_{1−x}S$ solid solutions // Thin Solid Films. 2004. V.461. P. 325–335.

25. Markov V.F., Tretyakova N.A., Maskaeva L.N., Bakanov V.M., Muhamedzyanov H.N. Hydrochemical synthesis, structure, semiconductor properties of films of substitutional $Pb_{1−x}Sn_xSe$ solid solutions // Thin Solid Films. 2012. Vol. 520. Iss. 16. P. 5227-5231.

26. Markov V.F. Maskaeva L.N. Calculating the boundary conditions of the formation of solid-phase metal sulfides and selenides by deposition with thio- and selenourea // Journal of Physical Chemistry. 2010. V. 86 №8. P. 1421-1426 [in Russian].

27. Ivanov P.N. Maskaeva L.N. Markov V.F. Voronin V.I. Investigation of Hydrochemical Deposited Films of Substitution Solid Solutions in Pb(II)-Cu(I)-S System // Journal of surface investigation. X-ray, synchrotron and neutron techniques. 2003. №8. P. 85-91 [in Russian].

28. Butler J.N. Ionic equilibrium. - Moscow: Chemistry. 1973. 448 p.

29. Lurie Yu.Yu. Handbook of Analytical Chemistry. - Moscow: Chemistry. 1989. 448 p.

30. Krasnopyorova A.P., Belikov K.N., Sofronov D.S. // Methods and objects of chemical analysis. 2013. Vol. 8. № 4. P. 194-198 [in Russian].

31. Belyaev A.P. Rubets V.P. Nuzhdin M.Yu. Kalinkin I.P. The influence of distinctly non-equilibrium conditions on the stoichiometry of the layer of cadmium telluride obtained by condensation from vapor phase // Semiconductors. 2003. Vol. 37(6). P. 641-643 [in Russian].

32. Valeev R.G. Beltukov A.N. Gilmutdinov F.Z. EXAFS spectroscopy study of the atomic structure of ZnS nanocomposite thin films // Journal of Structural Chemistry. 2011. Vol. 52 (7). P. 184-188 [in Russian].