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QUANTUM-CHEMICAL MODELING OF THE CHEMISTRY PROCESS OF THE ZINC SULFIDE AND ZINC SELENIDE FILMS SYNTHESIS

The quantum-chemical modeling of the synthesis process chemistry of ZnS and ZnSe in aqueos solutions was carried out. For modeling the simulation of ZnS synthesis was made through the formation of Zn(II) complex forms with the trisodium citrate, sodium hydroxide and the pair of ammonium hydroxide with hydrazine hydrate. For the synthesis of ZnSe was used only sodium hydroxide. It was established that this process passes through several intermediate stages with the transitional reactive complexes formation. On the basis of obtained data, the energy stages diagrams are constructed and the comparison of ZnS and ZnSe synthesis processes with various complexing agents is presented. The ZnS and ZnSe films were obtained by chemical synthesis method from an aqueous solution of zinc salt, complexing and chalcogenizing agents. X-ray phase analysis confirmed the formation of desired compounds, as well as the formation of ZnO in the case of ammonium hydroxide – hydrazine hydrate usage at the synthesis of ZnS films.

Key words: zinc sulfide, zinc selenide, thin films, quantum-chemical modeling, semiempirical methods, semiconductors.

Introduction

Semi-empirical method of quantum chemistry is one of the modeling reactions methods between molecules and substances by quantum-chemical calculations [1–3]. In Refs. [4–6], the theoretical basis of metal sulfides films formation from aqueous solution were described. Among the main factors affecting the course of the reaction, the following can be distinguished:

1. Concentration of initial reagents of the solution from which depositionismade and the physical parameters of the process (temperature, synthesis duration, etc.);

2. Nature of complexing and chalcogenizing reagents that surround the metal ion and generate chalcogen ions during the synthesis, respectively;

3. Nature of the substrate surface on which the films are formed.

It was noted [4] that during the synthesis process, the formation of transitional molecular reactive complexes (TMRC), associates, cluster and colloidal forms were possible in the working solution due to cooperation and fluctuation phenomena, which occur between the liquid and solid phases (newly formed the reaction product and substrate) at a short distance from the latter.

For the some metals ions (Me = Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}), the formation of complexes with thiourea of $[Me((NH_2)_2CS)_4]^{2+}$ type was established [4, 7]. From the reference data [4], the value of the stability constant of such zinc complex is very small (often absent in reference books),which does not apply to the mentioned above metals. So it is logical to assume the formation of intermediate complexes of $[L_n \cdots Zn \cdots (NH_2)_2CS]$ type, where zinc is coordinated on the one hand by ligands of the complexing agent, and on the other by thiourea. The decomposition process of such intermediate complexes, as a rule, involves the formation of molecular forms, and then monomolecular layers of zinc chalcogenide. To reduce the formation of by-products, it is necessary to create conditions in which the supply of zinc- and chalcogen-containing agents will be the same. It is also worth noting that some complexing agents perform only one function – the formation of a complex with metal. In this case, it is

necessary to add an additional pH regulator to ensure the stability and reactivity of the complex. Other complexing agents are able tofulfill two functions at the same time – to coordinate the metal ion and create the required hydrogen index of the solution.

Aim of the work

The aims of the present study are the following: 1. Implementationofquantum-chemical modeling of the ZnS and ZnSe synthesis processes withtheuseof PM7 method in MOPAC 2012 software package. This could be made on the basis of the hypothesis about the possibility of formation of transient reactive complexes, associates, clusters, structures of colloidal nature, which are structural units during the synthesis of zinc chalcogenide films due to the effects of co-operation and fluctuation in the working solution. 2. Comparison of the obtained results of ZnS and ZnSe simulations with the investigated properties of respective films. 3. Feasibility and efficiency evaluation of the synthesis in observed systems.

Materials and research methods

Modeling and calculations of the system energy change (ΔE) for the synthesis stages of zinc sulfide and zinc selenide were carried out by the semi-empirical method PM7 [8] with the use of MOPAC 2012 software package [9] and the Winmostar graphical interface [10].

The synthesis of ZnS films was carried out from a working solution prepared by mixing aqueous solutions of zinc chloride ($ZnCl_2$), complexing agent, thiourea ($(NH_2)_2CS$) and, if necessary, the pH regulator. Solutions of trisodium citrate ($Na_3C_6H_5O_7$), sodium hydroxide (NaOH), and a pair of ammonium hydroxide (NH_4OH) with hydrazine hydrate ($N_2H_4·H_2O$) were used as complexing agents. The exact synthesis parameters of ZnS films are given in ref. [11].

The synthesis of ZnSe films was carried out from a working solution prepared by mixing aqueous solutions of zinc chloride ($ZnCl_2$), sodium hydroxide and elemental selenium (Se) dissolved therein with the presence of hydrazine hydrate. The exact synthesis parameters of ZnS films are given in ref. [12, 13].

The X-ray diffraction patterns of deposited ZnS and ZnSe films samples were performedwith the use of DRON-3.0 diffractometer (Cu $K\alpha^-$radiation). The primary treatment of films diffractogram for the identification of phases was carried outby using Powder Cell program [14].

Results and discussion

The results of quantum chemical modeling of the ZnS and ZnSe films synthesis chemistry in aqueous solutions with various complexing agents by semi-empirical methods are presented in table 1. The geometry of starting zinc complexes are illustratedin Fig. 1–3.

Quantum-chemicalmodelingof ZnS synthesis chemistry with $Na_3C_6H_5O_7$.

Initially, when mixing solutions of zinc salt and trisodium citrate, a soluble $[Zn(C_6H_5O_7)]^-$ complex is formed (Fig. 1), where citrate ion plays the role of a ligand.

As can be seen from the conducted quantum-chemical modeling(table. 1, no. 1, stages 1–3) that after adding thiourea and a small amount of pH regulator to the solution, the $[(NH_2)_2CS\cdots Zn(OH)_2(C_6H_5O_7)]^{3-}$ TMRC is formed in the early stages of deposition. In the TMRC the Zn atom is coordinated with the S atom (Fig. 4). This process is accompanied by a slight endoeffect, that is, energy absorption.

Next, starting from stage 3 to stage 6, the formed complex undergoes rearrangement of two hydrogen atoms of $(NH_2)_2CS$ with two hydroxyl groups and detaching of two water molecules. As a result, $[(N_2H_2CS\cdots Zn(C_6H_5O_7)]^{3-}$ TMRC is formed. The result of these stages is a decrease in total energy of the system.

At the last stage, which is the most energy-intensive, the newly formed intermediate complex decomposed with the formation of zinc sulfide, citrate ion and cyanamide (stages 6–7).

During deposition process, the citrate ion ($C_6H_5O_7^{3-}$) does not change its structure and performs only a ligand role.

Quantum-chemicalmodelingof ZnS synthesis chemistry with NaOH.

In the case of mixing of a zinc salt solution with an excess of sodium hydroxide solution, which is a complexing agent and pH regulator at the same time, a soluble complex of tetratrahydroxozincate ($[Zn(OH)_4]^{2-}$) is formed (Fig. 2).

As can be seen from the performed modeling (table 1, no. 2, stages 1–2) that TMRC $[(NH_2)_2CS\cdots Zn(OH)_4]^{2-}$ is formed at the beginning of the deposition, after the addition of thiourea in the working solution (Fig. 5). InthisTMRC, the zinc atom is coordinated with the sulfur atom of the thiourea, with a slight increase in system energy.

15

Table 1

Modeled stages of ZnS and ZnSe films synthesis and energy stages diagrams

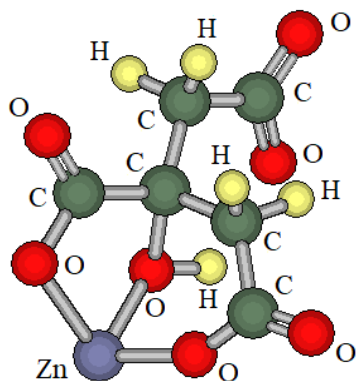| No.	Film	Complexing agent	Energy stages diagrams	Modeled stages
1	ZnS	$Na_3C_6H_5O_7$		Stages 1→3: $[Zn(C_6H_5O_7)]^- + 2OH^- + (NH_2)_2CS \rightarrow$ $\rightarrow [(NH_2)_2CS\cdots Zn(OH)_2(C_6H_5O_7)]^{3-}$; Stages 3→6: $[(NH_2)_2CS\cdots Zn(OH)_2(C_6H_5O_7)]^{3-} \rightarrow$ $\rightarrow [(N_2H_2CS\cdots\cdots Zn(C_6H_5O_7)]^{3-} + 2H_2O$; Stages 6→7: $[(N_2H_2CS\cdots Zn(C_6H_5O_7)]^{3-} \rightarrow ZnS\downarrow +$ $+ C_6H_5O_7^{3-} + CH_2N_2$.
2	ZnS	NaOH		Stages 1→2: $[Zn(OH)_4]^{2-} + (NH_2)_2CS \rightarrow$ $\rightarrow [(NH_2)_2CS\cdots Zn(OH)_4]^{2-}$; Stages 2→5: $[(NH_2)_2CS\cdots Zn(OH)_4]^{2-} \rightarrow$ $\rightarrow [(N_2H_2CS\cdots Zn(OH)_2]^{2-} + 2H_2O$; Stages 5→6: $[(N_2H_2CS\cdots Zn(OH)_2]^{2-} \rightarrow$ $\rightarrow [S\cdots Zn(OH)_2]^{2-} + CH_2N_2$; Stages 6→7: $[S\cdots Zn(OH)_2]^{2-} \rightarrow ZnS\downarrow + 2OH^-$.
3	ZnS	$NH_4OH + N_2H_4\cdot H_2O$		Stages 1→2: $[Zn(NH_3)_4]^{2+} + 2OH^- \rightarrow Zn(OH)_2 +$ $+4NH_3\uparrow$; Stages 2→3: $Zn(OH)_2 + (NH_2)_2CS \rightarrow$ $\rightarrow [(NH_2)_2CS\cdots Zn(OH)_2]$; Stages 3→7: $[(NH_2)_2CS\cdots Zn(OH)_2] \rightarrow$ $\rightarrow ZnS\downarrow + CH_2N_2 + 2H_2O$; By-process: $Zn(OH)_2 \rightarrow ZnO + H_2O$.
4	ZnSe	NaOH		Stages 1→2: $[Zn(OH)_4]^{2-} + Se^{2-} \rightarrow [Se\cdots Zn(OH)_4]^{4-}$; Stages 2→3: $[Se\cdots Zn(OH)_4]^{4-} \rightarrow ZnSe\downarrow + 4OH^-$.

16

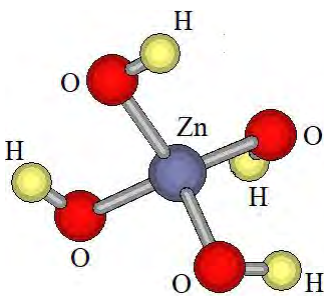*Fig. 1. The modeled $[Zn(C_6H_5O_7)]^-$ complex*

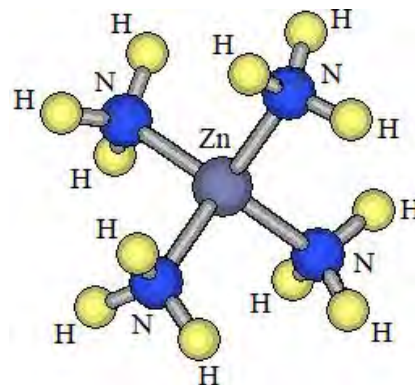

Fig. 2. The modeled $[Zn(OH)_4]^{2-}$ complex

Fig. 3. The modeled $[Zn(NH_3)_4]^{2+}$ complex

At the next stages 2–5, transition states occur when the hydrogen atoms rearrange and transfer from thiocarbamide to tetrahydroxozincate. As a result, two water molecules (stages 3–5) are detached from the $[(NH_2)_2CS \cdots Zn(OH)_4]^{2-}$ TMRC with the appearance of a new $[(N_2H_2CS \cdots Zn(OH)_2]^{2-}$ TMRC. The outcome of these stages is a decrease in the total energy of the system.

Further (stages 5–6), this intermediate complex decomposed with the formation of cyanamide and an intermediate phase – zinc dihydroxosulfide $[S \cdots Zn(OH)_2]^{2-}$, which is also accompanied by a decrease in the total energy of system.

At the last stages 6–7, $[S \cdots Zn(OH)_2]^{2-}$ decomposes into insoluble zinc sulfide and two hydroxyl groups, and the stages themselves are the most energy-intensive.

Quantum-chemical modeling of ZnS synthesis chemistry with NH_4OH and $N_2H_4 \cdot H_2O$.

Zinc can form with complexing agents of NH_4OH and $N_2H_4 \cdot H_2O$ the water-soluble complexes of zinc tetraammonia $[Zn(NH_3)_4]^{2+}$ and zinc tetrahydrazine $[Zn(N_2H_4)_4]^{2+}$, respectively.

Since, according to reference data [15], the value of stability constant for the zinc complex with ammonia ($pK^{1-4} = 9.08$) is almost five orders higher than with hydrazine ($pK^{1-4} = 3.84$), thenthe $[Zn(NH_3)_4]^{2+}$ complex form (Fig. 3) will be present in the working solution.

It can be seen from the modeling (table 1, no. 3, stages 1–2) that ZnS deposition is preceded by the stage of nucleation of the zinc hydroxide $(Zn(OH)_2)$ phase.

With increasing system energy, the complex $[Zn(NH_3)_4]^{2+}$ decomposes to $Zn(OH)_2$ and the ammonia as volatile compound evaporates from the working solution. This reduces the NH_4OH concentration during the process of ZnS synthesis.

As a consequence, the pH value decreases, which promotes the formation of zinc hydroxide. The decomposition of $Zn(OH)_2$, during the passage of the main process, will probably lead to the appearance of the zinc oxide (ZnO) phase as a by-product of the reaction. This may have happen at conditions, given in ref. [11]. The two water molecules are detach from $Zn(OH)_2$ and it transforms to ZnO (table 1, no. 3, by-process).

In the subsequent stages, thiourea is combined with the newly formed $Zn(OH)_2$ (stages 2–3). This produces the $[(NH_2)_2CS \cdots Zn(OH)_2]$ TMRC (Fig. 6).

After that, during the further heating (stages 3–7) the intermediate complex undergoes to rearrangement of hydrogen atoms with detaching of water molecules and destruction into cyanamide molecules and insoluble ZnS. Going to the last stage leads to a decrease in the total energy of the system, however, in the process of passing through the stages 3–7 there are local minimum and maximum of ΔE energy change.

Quantum-chemical modeling of ZnSe synthesis chemistry with NaOH.

Similarly to the synthesis of ZnS from a NaOH solution, in the case of ZnSe formation from hydroxide system, a soluble tetrahydroxy zincate $[Zn(OH)_4]^{2-}$ complex will form. Itsgeometry areillustrated in Fig. 3. The difference in this process will be the different nature of the chalcogenizing reagent, namely the generated Se^{2-} ions from elemental powdered selenium.

The results of quantum chemical modeling (Table 1, no. 4, stages 1–2) indicate that at the beginning of the deposition, selenium ion is coordinated with the zinc atom of tetrahydroxy zincate forming the $[Se \cdots Zn(OH)_4]^4$ TMRC (Fig. 7). This process requires the supply of energy to the system.

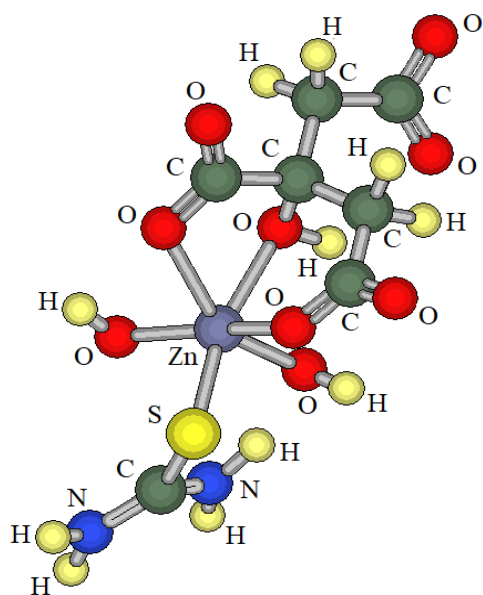17

Fig. 4. The modeled
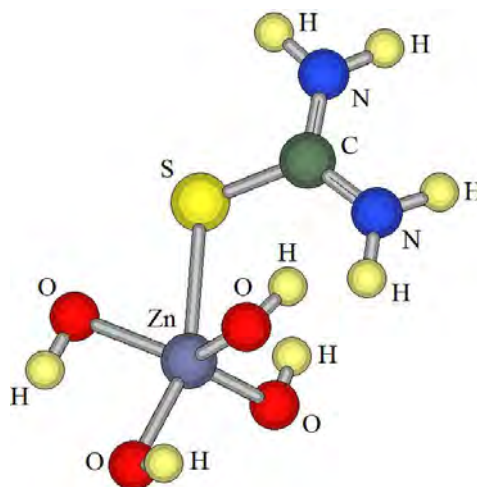$[(NH_2)_2CS\cdots Zn(OH)_2(C_6H_5O_7)]^{3-}$ *TMRC*

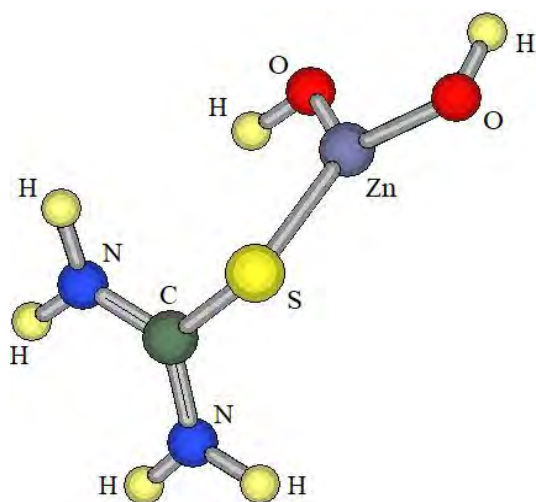*Fig. 5. The modeled*
$[(NH_2)_2CS\cdots Zn(OH)_4]^{2-}$ *TMRC*
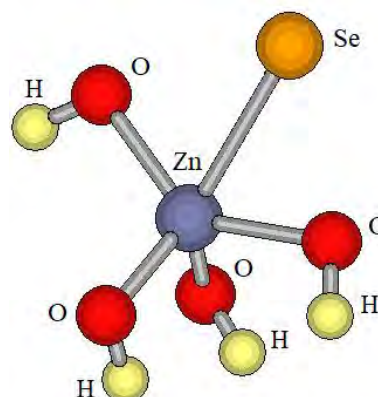

Fig. 6. The modeled $[(NH_2)_2CS\cdots Zn(OH)_2]$ TMRC

Fig. 7. The modeled ПРЗК$[Se\cdots Zn(OH)_4]^{4-}$ TMRC

Upon further heating of the reaction mixture (steps 2–3), the intermediate complex decomposed with the formation of insoluble zinc selenide and four hydroxide groups.

It is worth noting that in the case of obtaining the results of quantum-chemical calculations by the semiempirical PM7 method, their accuracy for the ZnSe formation process decreases, unlike for ZnS films, since the quantitative content of lighter atoms (H, C, O, N, S) in the modeled system decreases and the heavier ones (Zn, Se) grows. This increases the number of approximations performed in the calculations by semiempirical method [16].

According to quantum calculations (table 1), in all cases of ZnS and ZnSe synthesis, it is necessary to provide energy to start the initial stages and pass the energy barrier (the plot that connects the first two points on the energy diagrams). It reaches the highest value for ZnS synthesis with the use of NH_4OH and $N_2H_4\cdot H_2O$ complexing agents (197 kJ/mol). It is somewhat smaller for the ZnSe synthesis (105.6 kJ/mol) and the smallest for ZnS synthesis with the use of NaOH and $Na_3C_6H_5O_7$ (31.8 and 27.2 kJ/mol, respectively).

To verify the results of quantum-chemical modeling of ZnS and ZnSe obtaining, the ZnS and

18

ZnSe films were synthesized experimentally under modeled conditions. Their X-ray phase analysis was performed (Figs. 8, 9). It has been established that coatings contain the corresponding phases of cubic (sphalerite-type) modification. In all cases, the films were single-phase, except for the ZnS films synthesis with the use of ammonium hydroxide with hydrazine hydrate. Such samples containedtwo phases ZnO and ZnS, which was predicted by modeling ofthecorresponding case.
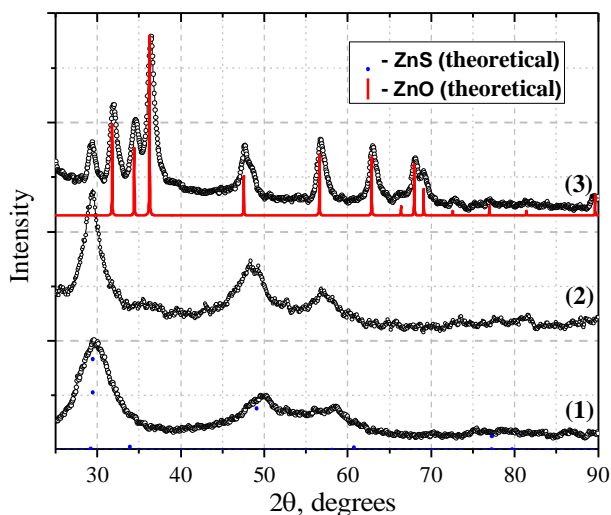

Fig. 8. The XRD patterns of ZnS films, obtained with the use of $Na_3C_6H_5O_7$ (1), NaOH (2), $NH_4OH+N_2H_4·H_2O$ (3) and thetheoretical diffraction patterns of ZnS i ZnO
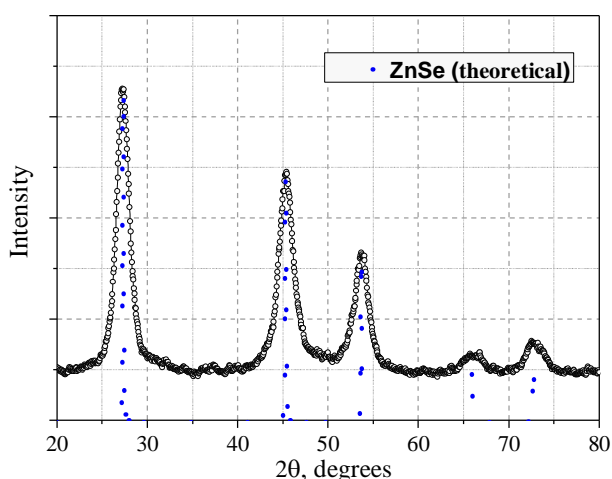

Fig. 9. The XRD pattern of ZnSe film, obtained with the use of NaOH the theoretical diffraction patterns of ZnSe

Conclusions

From the performed simulations and calculations for the four cases of zinc chalcogenides

formation, the NaOH complexing agent behaves energetically more profitably during the ZnS synthesis in the aggregate of all stages of synthesis reactions. However, according to the studies described in [17], it was established that when NaOH was used, the surface of the synthesized films consisted of spherical particles. Their contact area with the substrate surface is small.This results in weak adhesion to glass substrates and the ZnS layer could be removed by applying mechanical forces to the coating. Also, during prolonged synthesis, the upper film layer of ZnS spherical particles was partially washed out at cleaning of its surface by a jet of distilled water.

The ZnS formation reaction with the use of $Na_3C_6H_5O_7$ complexing agent is less energy profitable. However, the obtained ZnS coatings were characterized by a solid, smooth and mirror surface with good adhesion to glass substrates [11, 18]. With the increase in deposition duration, there was observed a linear region of increase in the films thickness with uniform growth over the entire substrate surface. The formation of spherical particles was not found, but only a small amount of surface defects. The ZnS contact area with the substrate is large, which explains the good adhesion. After depletion of the working solution, the number of conglomerates on the film surface increases and it begins cracking.

In the case of the use of NH_4OH and $N_2H_4·H_2O$ complexing agents,the zinc sulfide synthesis characterized by a tendency to form by-products [11, 19] and the deposition process itself is more energy-intensive than with the other complexing agents. This makes it impossible to use NH_4OH and $N_2H_4·H_2O$ for the production of film elements based on ZnS and ZnSe. The obtained sulfide films under similar conditions with another element of the zinc subgroup – cadmium did notcontain by-products [20, 21].

The ZnSe synthesis requiresmore energy for it formation than the synthesis of ZnS. This can be explained by a different nature of the chalcogenizing agent, which was used to obtain zinc selenide (Se^{2-}ions are negatively charged instead of electro-neutral $(NH_2)_2CS$). As a consequence, there is a need to overcome the repulsion between Se^{2-} and OH^- ions.

The synthesis of ZnS films was performed with the use of trisodium citrate, sodium hydroxide and a pair of ammonium hydroxide – hydrazine hydrate. For the ZnSe films synthesis only sodium hydroxide was used. The X-ray analysis confirmed the ZnS formation, as well as the ZnO formation duringthe synthesis of ZnS films withthe useof NH_4OH and $N_2H_4·H_2O$, which was predicted by the correspondingquantum-chemical modeling.

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КВАНТОВО-ХІМІЧНЕ МОДЕЛЮВАННЯ ХІМІЗМУ ПРОЦЕСУ СИНТЕЗУ ПЛІВОК ЦИНКУ СУЛЬФІДУ ТА ЦИНКУ СЕЛЕНІДУ

Проведено квантово-хімічне моделювання процесу синтезу ZnS та ZnSe у водних розчинах. Змодельовано синтез ZnS утворенням проміжних комплексних форм Zn(II) з тринатрій цитратом, натрій гідроксидом та парою амоній гідроксиду з гідразин гідратом. Під час синтезу ZnSe використано лише натрій гідроксид. Встановлено, що цей процес проходить через декілька проміжних стадій з утворенням перехідних реакційноздатних комплексів. На основі отриманих даних побудовано енергетичні діаграми стадій та здійснено порівняння процесів синтезу ZnS і ZnSe з різними комплексоутворювальними реагентами. Методом хімічного синтезу отримано плівки ZnS та ZnSe з водного розчину солі цинку, комплексоутворювального та халькогенізуючого реагентів. Рентгенофазовим аналізом підтверджено утворення цільових сполук, а також формування ZnO під час синтезу плівок ZnS з використанням амоній гідроксиду і гідразин гідрату.

Ключові слова: цинк сульфід, цинк селенід, тонкі плівки, квантово-хімічне моделювання, напівемпіричні методи, напівпровідники.