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

The HgS and HgSe films were obtained by chemical synthesis method from an aqueous solution of mercury(II) salt, complexing and chalcogenizing agents. For the obtaining of complex forms with Hg(II) the thiourea was used at the HgS synthesis, and potassium iodide, potassium rhodanide and sodium thiosulfate – at the HgSe synthesis. X-ray phase analysis was confirmed the formation of desired compounds, as well as the formation of $Hg_3I_2Se_2$ ternary compound in the case of potassium iodide use at the synthesis of HgSe films. The quantum-chemical modeling of the synthesis process chemistry of HgS and HgSe films was carried out. It is 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 HgS and HgSe synthesis processes with various complexing agents has been carried out.

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

Introduction

The quantum chemistry semi-empirical methods are one of the ways to simulate the reactions between molecules and substances with the help of quantum-chemical calculations [1]. In the works [2-5] the theoretical basis of the metals sulfide films formation from an aqueous solution are described. Among the main factors that affects on the reaction course are the following:

1. The concentration of the initial reagents of the solution from which the deposition is carried out, the physical parameters of the process (temperature, synthesis duration et al.);

2. The natures of complexing and chalcogenizing agents, which coordinates the metal ion and generate chalcogen ions during synthesis, respectively;

3. The nature of the surface on which the films formation takes place;

It was noted that formation of transitional molecular reactive complexes (TMRC), associates, clusters and colloid forms formation in the working solution is possible during synthesis due to co-operative and fluctuation phenomena. These phenomena take place between the liquid and solid phases (substrate, newly formed forms of reaction product) at the short distance from the last [4].

The possibility of $[Me((NH_2)_2CS)_4]^{2+}$ complexes formation with thiourea and certain metal ions (Me = Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}) were established [6], which could be used during the HgS films synthesis, where thiourea serves as chalcogenizing and complexing agent at the same time. In the case of other complexing agents using, it is logical to assume the possibility of passing a competing complexation process with the formation of $[L_{n-1}\cdots Hg\cdots(NH_2)_2CS]$ type TMRC. At this, the mercury atom coordinated, from one side, by ligands of the complexing agent, which was taken for synthesis, and from the other side – by $(NH_2)_2CS$.

The process of such complexes decomposition, as a rule, involves the molecular forms formation, and then monomolecular layers of mercury chalcogenides. It is also worth noting that some complexing agents performs mostly one function – binding of metal ion into complex. In this case, it is necessary to add, in addition, the pH regulator to ensure the stability and reactivity of complex. Some complexing agents can perform two functions – the metal ion coordination and creation of required pH-value of the working solution at the same time.

Aim of the work

Implementation of quantum-chemical modeling of the HgS and HgSe films synthesis processes by PM6 or PM7 method in the MOPAC 2012 program package based on the hypothesis about the possibility of formation of transitional reactive complexes, associates, clusters, structures with colloidal nature and which are structural links in the process of mercury(II) chalcogenides films synthesis due to co-operative and fluctuation phenomena in the working solution.

Materials and research methods

For the HgS films synthesis, freshly prepared aqueous solutions of mercury(II) nitrate ($Hg(NO_3)_2$), and thiourea (($NH_2)_2CS$) were used. The thiourea was used as complexing and chalcogenizing agent at the same time [7].

For the HgSe films synthesis, freshly prepared aqueous solutions of mercury(II) nitrate, complexing agent and sodium selenosulfate (Na_2SeSO_3) were used. As complexing agents were used solutions of potassium iodide (KI), potassium rhodanide (KSCN) and sodium thiosulphate ($Na_2S_2O_3$) [8].

The synthesis of HgS and HgSe films were carried out at 90 °C and at 20 °C, respectively, on pre-cleaned glass substrates.

The X-ray diffraction (XRD) analysis of deposited HgS and HgSe films samples were performed using DRON-3.0 diffractometer (Cu $K\alpha^-$ radiation). The primary treatment of films diffractogram for the identification of phases was conducted by using PowderCell program [9].

The modeling and calculation of the HgS synthesis stages and energy effects of each stage was done by PM7 [10] and HgSe – by PM6 [11] semi-empirical method in the MOPAC 2012 program package [12] and Winmostar graphical interface [13].

Results and discussion

The X-ray phase analysis of HgS film was performed (Fig. 1, Fig. 2). It was established that the coatings are single-phase and contain HgS in the trigonal modification (HgS structural type, cinnabar).
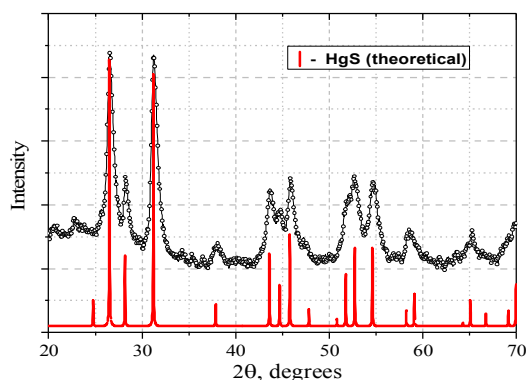

Fig. 1. The XRD pattern of HgS film, obtained with the use of ($NH_2)_2CS$ and theoretical diffraction pattern of HgS

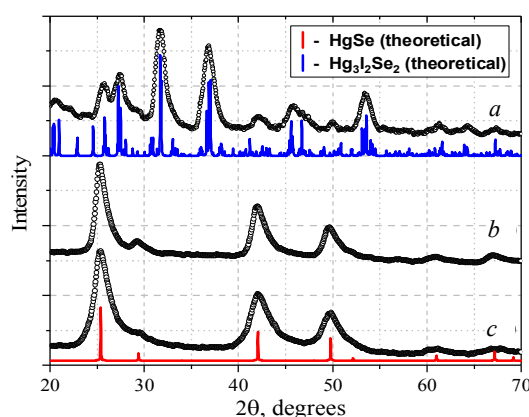*Fig. 2. The XRD patterns of HgSe films, obtained with the use of KI (a), KSCN (b), $Na_2S_2O_3$ (c) and theoretical diffraction patterns of HgSe and $Hg_3I_2Se_2$*
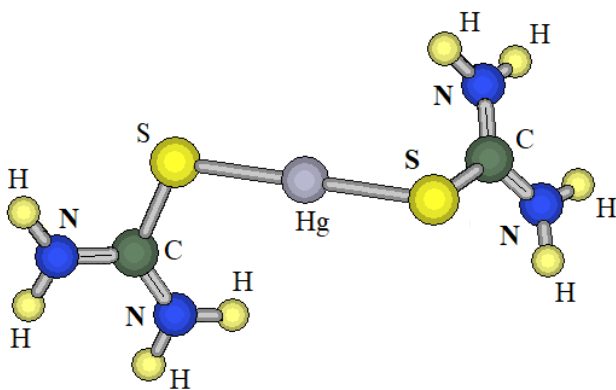
Fig. 3. The modeled [(($NH_2)_2CS)_2Hg]^{2+}$ complex
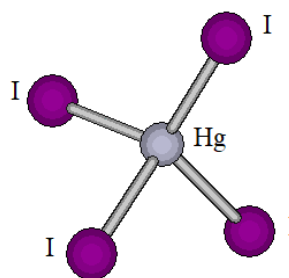
Fig. 4. The modeled $[HgI_4]^{2-}$ complex

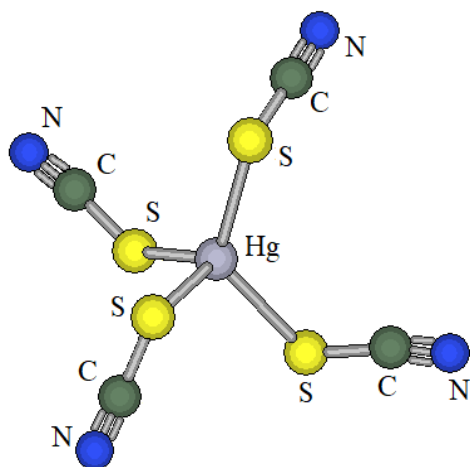В. Є. Стаднік, М. А. Созанський, П. Й. Шаповал, Р. Р. Гумінілович, Й. Й. Ятчишин

Fig. 5. The modeled [Hg(SCN)$_4$]$^{2-}$ complex
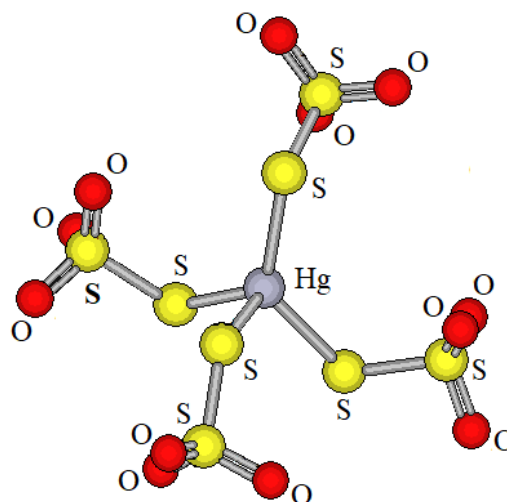

Fig. 6. The modeled [Hg(S$_2$O$_3$)$_4$]$^{6-}$ complex

The HgSe films are single-phase of cubic modification (structural type ZnS, sphalerite) when KSCN and Na$_2$S$_2$O$_3$ were used. In the case of KI using the films are double-phased and consist of cubic HgSe and the ternary compound of mercury-iodide-selenide (Hg$_3$I$_2$Se$_2$) of monoclinic modification (structure type Hg$_3$Br$_2$S$_2$).

In Table 1 were presented the results of quantum chemical modeling of the HgS and HgSe films synthesis chemistry in aqueous solutions with various complexing agents by semi-empirical methods. The geometry of starting mercury(II) complexes are shown on Fig. 3-Fig. 7.

Quantum-chemical modeling of HgS films synthesis chemistry with (NH$_2$)$_2$CS

At mixing a solution of mercury(II) salt with a double excess of (NH$_2$)$_2$CS, a soluble [((NH$_2$)$_2$CS)$_2$Hg]$^{2+}$ complex has been formed, where thiourea acts as a ligand of complexing agent. It should be noted that the best quality of HgS films can only be obtained by using complex with coordination number (CN) = 2. After adding of the pH regulator, an excess of OH$^-$-ions, which was created in the solution, interact with [((NH$_2$)$_2$CS)$_2$Hg]$^{2+}$ complex with the formation of TMRC [((NH$_2$)$_2$CS)$_2$Hg(OH)$_2$] with CN = 4 (Fig. 7). The next intra-molecular rearrangement of two hydrogen atoms from one NH$_2$-group of thiourea to the two hydroxyl groups leads to detach of two water molecules and cyanamide with the formation of

[((NH$_2$)$_2$CS)HgS] complex. Due to its following decomposition, the formation of HgS occurs.

Quantum-chemical modeling of HgSe films synthesis chemistry with KI.

In the case of mixing the excess of KI with mercury(II) salt, the formation of [HgI$_4$]$^{2-}$ complex occurs, which in the presence of SeSO$_3$$^{2-}$-ions, transforms to TMRC [I$_3$Hg···SeSO$_3$]$^{3-}$ (Fig. 8). The last decomposes under the OH$^-$ action with the formation of a new intermediate complex [I$_3$Hg···Se]$^{3-}$ and SO$_4$$^{2-}$ ion. At the next stage [I$_3$Hg···Se]$^{3-}$ destructs with the formation of HgSe solid phase.

Quantum-chemical modeling of Hg$_3$I$_2$Se$_2$ ternary compound synthesis chemistry with KI.

At the initial stage of synthesis, as in the case of the HgSe film formation with KI, the formation of [HgI$_4$]$^{2-}$ occurs. Next, the interaction of [HgI$_4$]$^{2-}$ complex with the newly formed mercury selenide take place with the formation of [HgSe···HgI$_2$] TMRC. At the stage 3, the I$^-$ ion, which was displaced from the initial [HgI$_4$]$^{2-}$ complex, binds to the Hg atom of mercury selenide, which is a part of [HgSe···HgI$_2$], and form new [I···HgSe···HgI$_2$]$^-$ intermediate complex. At stages 4-5, the interaction of [I···HgSe···HgI$_2$]$^-$ complex with the newly formed HgSe and the intra-molecular rearrangement of second I$^-$ ion, which remained from the initial complex [HgI$_4$]$^{2-}$ take place with the formation, as a result, of [I···HgSe···Hg···SeHg···I] structure ternary compound.

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Table 1

Modeled stages of HgS and HgSe films synthesis and energy stages diagram

Film	Complexing agent	Energy stages diagram	Modeled stages
HgS	$(NH_2)_2CS$		Stage 1→2: $[((NH_2)_2CS)_2Hg]^{2+} + 2OH^- \rightarrow$ $\rightarrow [((NH_2)_2CS)_2Hg(OH)_2]$; Stage 3→5: $[((NH_2)_2CS)_2Hg(OH)_2] \rightarrow$ $\rightarrow [((NH_2)_2CS)HgS] + 2H_2O + CN_2H_2$; Stage 6: $[((NH_2)_2CS)HgS] \rightarrow HgS\downarrow + (NH_2)_2CS$.
HgSe	KI		Stage 1→2: $[HgI_4]^{2-} + SeSO_3^{2-} \rightarrow [I_3Hg\cdots SeSO_3]^{3-} + I^-$; Stage 3→4: $[I_3Hg\cdots SeSO_3]^{3-} + 2OH^- \rightarrow$ $\rightarrow [I_3Hg\cdots Se]^{3-} + SO_4^{2-} + H_2O$; Stage 5: $[I_3Hg\cdots Se]^{3-} \rightarrow HgSe\downarrow + 3I^-$.
$Hg_3I_2Se_2$ (co-product)			Stage 1→2: $[HgI_4]^{2-} + HgSe \rightarrow [HgSe\cdots HgI_2] + 2I^-$; Stage 3: $[HgSe\cdots HgI_2] + I^- \rightarrow [I\cdots HgSe\cdots HgI_2]^-$; Stage 4→5: $[I\cdots HgSe\cdots HgI_2]^- + HgSe \rightarrow$ $\rightarrow [I\cdots HgSe\cdots HgI\cdots SeHg] + I^-$; Stage 6: $[I\cdots HgSe\cdots HgI\cdots SeHg] \rightarrow$ $\rightarrow [I\cdots HgSe\cdots Hg\cdots SeHg\cdots I]\downarrow$.
HgSe	KSCN		Stage 1→2: $[Hg(SCN)_4]^{2-} + SeSO_3^{2-} \rightarrow$ $[(SCN)_3Hg\cdots SeSO_3]^{3-} + SCN^-$; Stage 3→4: $[(SCN)_3Hg\cdots SeSO_3]^{3-} + 2OH^- \rightarrow$ $[(SCN)_3Hg\cdots Se]^{3-} + SO_4^{2-} + H_2O$; Stage 5: $[(SCN)_3Hg\cdots Se]^{3-} \rightarrow HgSe\downarrow + 3SCN^-$.
HgSe	$Na_2S_2O_3$		Stage 1→3: $[Hg(S_2O_3)_4]^{6-} + SeSO_3^{2-} \rightarrow$ $\rightarrow [(S_2O_3)_3Hg\cdots SeSO_3]^{6-} + S_2O_3^{2-}$; Stage 4→5: $[(S_2O_3)_3Hg\cdots SeSO_3]^{6-} + 2OH^- \rightarrow$ $\rightarrow [(S_2O_3)_3Hg\cdots Se]^{6-} + SO_4^{2-} + H_2O$; Stage 6: $[(S_2O_3)_3Hg\cdots Se]^{6-} \rightarrow HgSe\downarrow + 3S_2O_3^{2-}$.
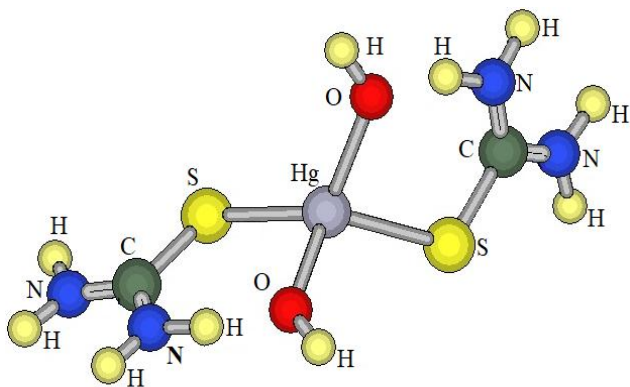
Fig. 7. The modeled [((NH₂)₂CS)₂Hg(OH)₂] TMRC.
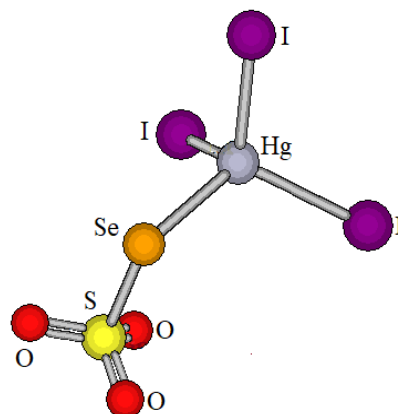
Fig. 8. The modeled [I₃Hg···SeSO₃]³⁻ TMRC.
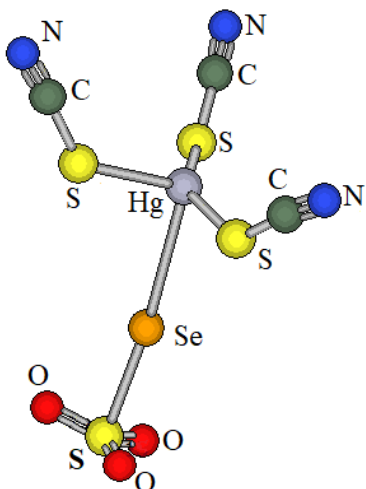
Fig. 9. The modeled [(SCN)₃Hg···SeSO₃]³⁻ TMRC.
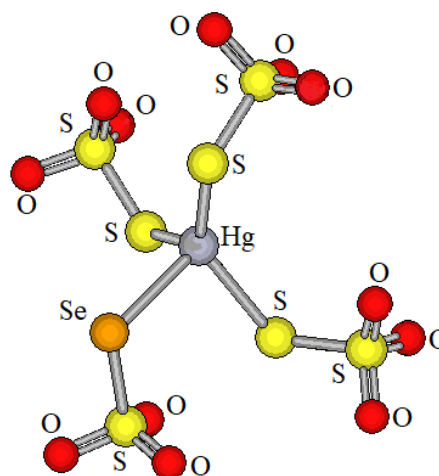
Fig. 10. The modeled [(S₂O₃)₃Hg···SeSO₃]⁶⁻ TMRC.

Quantum-chemical modeling of HgSe films synthesis chemistry with KSCN.

During the synthesis with potassium rhodanide, mercury(II)-ions in the solution are present in the form of $[Hg(SCN)_4]^{2-}$ complex. In the presence of $SeSO_3^{2-}$ ions in the working solution, the $[(SCN)_3Hg\cdots SeSO_3]^{3-}$ TMRC was formed (Fig. 9) due to the displacement of one SCN^- group from the composition of the previous complex. In alkaline medium, the $SeSO_3^{2-}$ group under the OH^--ions action decomposes with the formation of SO_4^{2-} ion and a new $[(SCN)_3Hg\cdots Se]^{3-}$ TMRC. The decomposition of the last leads to formation of the required product.

Quantum-chemical modeling of HgSe films synthesis chemistry with Na₂S₂O₃.

At mixing mercury(II) salt with the excess of sodium thiosulfate, a soluble $[Hg(S_2O_3)_4]^{6-}$ complex was formed. In the presence of $SeSO_3^{2-}$ ions, the $[(S_2O_3)_3Hg\cdots SeSO_3]^{6-}$ TMRC (Fig. 10) occurs due to the displacement of one $S_2O_3^{2-}$ group from initial complex. In an alkaline medium, the $SeSO_3^{2-}$ group decomposes under the OH^- ions action with the formation of a new TMRC – $[(S_2O_3)_3Hg\cdots Se]^{6-}$. The formation of low soluble HgSe compound take place due to the decomposition of the last complex.

On the basis of obtained data from quantum-chemical modeling by the semiempirical methods the energy stages diagrams of HgS, HgSe and Hg₃I₂Se₂ synthesis are constructed and given in Table 1. In all cases (except for the HgSe synthesis with Na₂S₂O₃ and KSCN), the passage of the initial stages occurs with the decrease of system energy, which is the largest in the case of HgS synthesis with (NH₂)₂CS and Hg₃I₂Se₂ synthesis with KI and equals to 204.2 kJ/mol and 204.06 kJ/mol, respectively. For HgSe synthesis with KI and KSCN, the system needs to take a small amount of energy, which is equal to 32.82 and 51.64 kJ/mol, respectively. The differences of the next stages passage energetic character are observed, which leads to final product formation.

In the case of the HgS synthesis with $(NH_2)_2CS$, ΔE between the initial and final stages is 119 kJ/mol, indicating the necessity to perform synthesis at elevated temperature. The passage from stage 1 to step 2 accompanied by system energy decrease, which corresponds to the transition of the $[((NH_2)_2CS)_2Hg]^{2+}$ complex to more stable complex of $[((NH_2)_2CS)_2Hg(OH)_2]$. The system passage from stage 2 to step 5 occurs with a slight decrease in the system energy ($\Delta E \sim 50$ kJ/mol). However, for the stage 4 passage, which corresponds to the detachion of one water molecule as a result of the intramolecular rearrangement of the hydroxyl group, the system energy slightly increases due to the intermediate complex formation with a non-characteristic for Mercury CN = 3. The passage from stage 5 to stage 6 occurs with a significant increase of the system energy ($\Delta E \sim 120$ kJ/mol), which can be explained by system transition from homogeneous to heterogeneous due to the formation of a low-soluble HgS.

From the performed modeling and calculations for the synthesis of HgSe films and $Hg_3I_2Se_2$ compound with different complexing agents, the ΔE differs between the initial and final stages and varies from ~ 455 kJ/mol (for HgSe synthesis from with $Na_2S_2O_3$) to ~ 550 kJ/mol (for $Hg_3I_2Se_2$ synthesis with KI). Such differences in the system energy value compared to the case of the HgS synthesis with $(NH_2)_2CS$ can be explained by the different nature of the chalcogenizing and complexing agents ions ($SeSO_3^{2-}$ and $L^{i-} = S_2O_3^{2-}$, I^- та SCN^- ions charged negatively). The last form negatively charged complexes with the Hg^{2+} ion and, as a result, the necessity to overcome the electrostatic repulsion between the $SeSO_3^{2-}$ ions, OH^- groups and mercury complex ions. The hydrolysis of the $SeSO_3^{2-}$ group with the release of Se^{2-} is impossible without OH^- groups. The modeled chemistry of HgSe synthesis with the use of proposed complexing reagents are similar. It's because in all cases, the one ligand of the complexing agent is replaced by $SeSO_3^{2-}$ ion, which hydrolyzes in an alkaline medium with HSO_4^- detach. The decomposition of newly formed $[L_3Hg\cdots Se]^{3i-}$ leads to formation of the required product (HgSe). Such similarity illustrated in the energy stages diagrams of HgSe synthesis. However, with the use of $Na_2S_2O_3$ and KSCN use it is necessary to overcome the energy barrier for next stages passage be each system. For decomposition of $[L_3Hg\cdots Se]^{3i-}$ TMRC with the HgSe formation (with the KI and KSCN use) it is necessary to provide a small amount of energy to system to ensure the it transition from homogeneous to heterogeneous.

By comparing the energy effect of the HgSe synthesis processes, the significantly higher ΔE value, than for HgS synthesis with $(NH_2)_2CS$, indicates the possibility of HgSe synthesis at lower temperatures, what was confirmed in practice. Considering that the system energy change is somewhat higher in the case of $Hg_3I_2Se_2$, than in the case of the synthesis of HgSe films with the same complexing agent, the formation of ternary compound at room temperature, as a co-product, can be explain. This is because the difference of system energy, under the synthesis conditions, is insignificant, and that's why the formation of a mixture of these compounds is take place.

Conclusions

On the basis of the performed work, the following summation were made:

The main factors that influencing on the metal sulfides films formation during their chemical synthesis from aqueous solution were described.

The X-ray phase analysis confirmed the HgS compound formation with the use of $(NH_2)_2CS$ complexing agent and HgSe with the use of KI, KSCN and $Na_2S_2O_3$. A $Hg_3I_2Se_2$ ternary compound is formed, in addition to the HgSe, in the KI system.

On the basis of literature data analysis are proposed the hypothesis about the formation of intermediate, reactive complexes, associates, clusters, structures with colloidal nature and which are structural links in the process of mercury chalcogenides film synthesis due to co-operative and fluctuation phenomenas in the working solution.

For the first time a quantum-chemical modeling of synthesis chemistry chemistry of HgS films with the use of $(NH_2)_2CS$ and HgSe films with the use of KI, KSCN and $Na_2S_2O_3$ was carried out on the basis of the proposed hypothesis.

The comparison of HgS and HgSe synthesis processes with various complexing agents based on the calculated energy stages diagrams of the modeled chemistry by semi-empirical methods in MOPAC2012 program package has been made.

It was found that the HgS films synthesis with $(NH_2)_2CS$ should be carried out at elevated temperatures, as a result of the smaller system energy change ($\Delta E = 119$ kJ/mol) compared to ΔE for the HgSe films synthesis ($\Delta E = 450$–550 kJ/mol). A larger value of a system energy change for $Hg_3I_2Se_2$ synthesis ($\Delta E = 550$ kJ/mol) as compared

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to HgSe films deposition (ΔE = 438 kJ/mol) at the KI use as a complexing agent, indicates the possibility of both products forming. This has been confirmed experimentally. A similar nature of the system energy change and the proximity of ΔE values of the modeling stages of HgSe films synthesis with the use of different complexing agents (ΔE = 430–550 kJ/mol) indicates the same chemistry of their synthesis.

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

Методом хімічного синтезу отримано плівки HgS та HgSe із водного розчину солі меркурію(II), комплексоутворювального та халькогенізуючого реагентів. Для отримання комплексних форм з Hg(II) використано тіокарбамід при синтезі HgS, а калій йодид, калій роданід та натрій тіосульфат – при синтезі HgSe. Рентгенофазовим аналізом підтверджено утворення цільових сполук, а також формування тернарної сполуки Hg₃I₂Se₂ при синтезі плівок HgSe з використанням калій йодиду. Проведено квантово-хімічне моделювання хімізму процесу синтезу плівок HgS та HgSe. Встановлено, що цей процес має декілька проміжних стадій із утворенням перехідних реакційноздатних комплексів. На основі отриманих даних побудовано енергетичні діаграми стадій та порівняно процеси синтезу HgS і HgSe із різними комплексоутворювальними реагентами.

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