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SYNTHESIS OF CADMIUM SULFIDE THIN FILMS FROM AN AQUEOUS SOLUTION CONTAINING SODIUM CITRATE

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The cadmium sulfide (CdS) films were prepared on glass substrates by chemical bath deposition method using aqueous solutions of cadmium chloride, thiourea, sodium citrate (complexing agent) and ammonia (pH regulator). A theoretical calculation of the boundary conditions of the formation of cadmium sulfide and cadmium hydroxide in the citrate-ammonia system was performed in this work. The composition, structure, optics and morphology of the synthesized CdS semiconductor films were experimentally investigated. The obtained films are two-phase and consist of CdS in both sphalerite and wurtzite modifications. They have a homogeneous solid surface, a practically stoichiometric composition and a narrow interval of the change of optical band gap. The quantum-chemical modeling of possible chemism of the CdS synthesis was performed. According to the results of the calculation, cadmium sulfide is formed from the initial cadmium citrate complex via the formation of several intermediate complexes. An analysis of the obtained experimental results allows finding the relationship between the deposition conditions and properties of the prepared semiconductor films, revealing the advantages of the use of sodium citrate as a complexing agent and determining the expediency of its application.

Keywords: cadmium sulfide, semiconductor film, chemical deposition, optical properties, morphology analysis.

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Introduction

Cadmium sulfide (CdS) is one of the most technologically important semiconductor materials of $A^{II}B^{VI}$ group since it has very suitable properties as a window layer of solar cell applications [1–3]. Chemical bath deposition (CBD) is a popular and effective way to obtain it [4]. This method is based on the synthesis of coatings at temperatures below 373 K from aqueous solution which consist of the metal salt, complexing agent, chalcogenizer and pH regulator if necessary.

Previously, the use of trisodium citrate was considered the most successful choice from several complexing agents for deposition of good quality zinc sulfide thin films [5]. Since cadmium is one of the members of zinc subgroup of metals, a synthesis of cadmium sulfide films from an aqueous solution of trisodium citrate can be also carried out. Study of the effect of this complexing agent and deposition duration may be performed, which will allow relating these parameters to the properties of the CdS films in order to obtain further high-quality coatings.

Experimental

Freshly prepared solutions of cadmium chloride ($CdCl_2$), ammonia (NH_3) as pH regulator, sodium citrate ($Na_3C_6H_5O_7$) as complexing agent and thiourea ($(NH_2)_2CS$) were used for the CBD of CdS films. The working solution was prepared from the sequential addition of these reagents: 10 mL of 0.1 M $CdCl_2$ solution, 2 mL of 14.28 M NH_3 solution, 2–40 mL of 0.5 M $Na_3C_6H_5O_7$ solution, 138 mL of distilled water and 10 mL of 1.0 M $(NH_2)_2CS$ solution. The total volume of the solution was 200 mL. The final concentrations of compounds in the working solution are given in Table 1. The deposition was carried out for 5–70 min at a temperature of 343 K. The pH of working solution was ca. 11.3.

The chemical bath deposition of CdS films was performed on pre-cleaned glass substrates (24×24 mm). The deposition was carried out in a glass bath, after which the substrates were removed, washed with distilled water and dried in air.

The possibility of adding 2 mL of 1.0 M NaOH

solution instead of 2 mL of 14.28 M NH_3 solution was considered. In this case, the pH of working solution was approximately the same, but CdS films were partially separated from the substrates during the synthesis or at the cleaning of coatings with distilled water, which was unpractical.

Table 1

The concentration of the compounds in the working solution for synthesis of CdS films

Compound	Concentration, M
$CdCl_2$	0.005
NH_3	0.14
$Na_3C_6H_5O_7$	0.005–0.10
$(NH_2)_2CS$	0.05

The synthesized samples of CdS films were yellow in color with a mirror hue. Their adhesion to the glass substrate was strong. The films couldn't be removed by applying mechanical efforts.

The X-ray diffraction analysis of deposited samples was performed using DRON-3.0 diffractometer (CuK_α radiation). The primary treatment of film diffractogram for the identification of phases was conducted by using PowderCell program [6]. The unit cell parameters were calculated by the FullProf software package [7]. The investigation of the film surface morphology was carried out using a scanning electron microscope REMMA-102-02 with a microanalysis system. The film thickness was measured using profilometer DEKTAK IIA (SLOAN). The optical transmission spectra of the films were recorded by Xion 500 «Dr. Lange» spectrophotometer in the wavelength range of 340–900 nm. The optical transmission accuracy was ±0.5%. The optical band gaps (E_g) were determined from $(\alpha \cdot h\nu)^2$ vs. hn dependencies by extrapolation of the linear parts of the $(\alpha \cdot h\nu)^2$ curves to the intersection with the energy axis. The modeling and calculation of geometrical parameters and enthalpies of the formation of CdS synthesis were done by PM7 semi-empirical method using MOPAC 2016 program [available at: http://openmopac.net/] and graphical interface Winmostar version 8.001 [available at: http://winmostar.com].

Results and discussion

The formation of cadmium complexes with citrate, ammonia and hydroxide are possible during the synthesis of CdS films. In such a system, the minimum concentration of cadmium salt required for the formation of solid CdS and $Cd(OH)_2$ phases was calculated by the following equations [8–10]:

$$pC^{min}_{Cd^{2+}} = pSP_{CdS} - p\alpha_{Cd^{2+}} - \left(pK^{1,2}_{H_2S} - 2pH + \right.$$
$$\left. + \frac{1}{2}pK_{(NH_2)_2CS} + p[(NH_2)_2CS] - p\frac{\beta_{H_2CN_2}}{\beta_{H_2S}}\right); \quad (1)$$

$$pC^{min}_{Cd^{2+}} = pSP_{Cd(OH)_2} + 2pH - p\alpha_{Cd^{2+}} - pK_{H_2O}, \quad (2)$$

where $\beta_{H_2S} = [H^+]^2 + K^1_{HS^-}[H^+] + K^{1,2}_{H_2S}$;

$$\beta_{H_2CN_2} = [H^+]^2 + K^1_{HCN_2^-}[H^+] + K^{1,2}_{H_2CN_2};$$

p is an indicator (negative decimal logarithm); $C^{min}_{Cd^{2+}}$ is the minimum concentration of cadmium ions required to the formation of a solid phase; SP_{CdS} is the solubility product of CdS; $K^{1,2}_{H_2S}$, $K^{1,2}_{H_2CN_2}$, $K_{(NH_2)_2CS}$, K_{H_2O} are the dissociation constants of hydrogen sulfide, hydrogen cyanamide, thiourea and water, respectively; $\alpha_{Cd^{2+}}$ is the molar fraction of the free Cd^{2+} ions in the solution.

The value of $\alpha_{Cd^{2+}}$ can be found from the following equation:

$$\alpha_{Cd^{2+}} = \frac{1}{1 + \frac{[L]}{K^1_L} + \frac{[L]^2}{K^{1,2}_L} + ... + \frac{[L]^n}{K^{1,2,...n}_L}}, \quad (3)$$

where [L] is the concentration of the free ligand of complexing agent; and $K^{1,2,...n}_L$ is the instability constants of the cadmium complexes with citrate, ammonia and hydroxide, respectively.

On the basis of equations (1) and (2), the dependences of the minimum concentration of cadmium salt required for the CdS and $Cd(OH)_2$ formation at different pH values of the working solution were plotted (Fig. 1). The calculations were carried out using the following initial values of compound concentrations: $[NH_3]$=0.14 M; $[Na_3C_6H_5O_7]$=0.10 M; $[(NH_2)_2CS]$=0.05 M. The other values of thermodynamic constants used in calculations were taken from the literature data [10,11].

It was impossible in practice to obtain coatings at the minimum calculated concentration (10^{-13} M at pH 13). The minimum concentration of the initial cadmium salt for the deposition of solid and uniform CdS thin films was 10^{-3} M. Reducing the concentration leads only to slight turbidity without film formation, which was unsuitable. Also by mixing $CdCl_2$ and NH_3 at the molar ratio of 1:28 (Table 1),

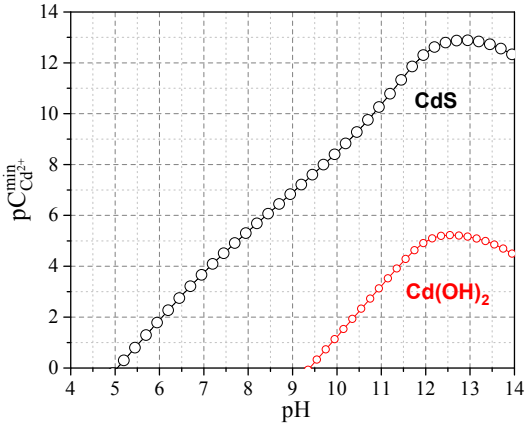

Fig. 1. The boundary conditions of the CdS and $Cd(OH)_2$ formation in the cadmium–citrate-ammonia system

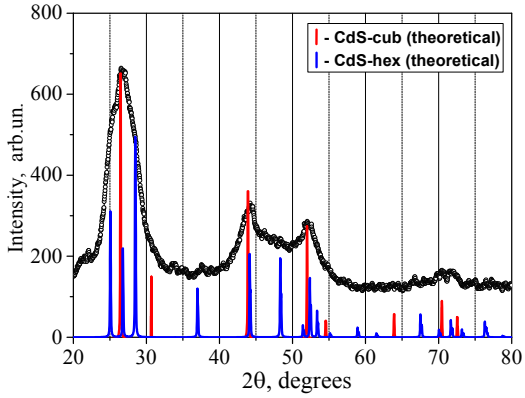

Fig. 2. The experimental X-ray diffraction profile of CdS film

the white turbidity of $Cd(OH)_2$ was formed instead of $[(NH_3)_4Cd]^{2+}$ or $[(NH_3)_6Cd]^{2+}$ complex. When $Na_3C_6H_5O_7$ was added to this solution, the turbidity disappeared due to the formation of cadmium citrate complex. In other way, without $Na_3C_6H_5O_7$, only at least 150-fold excess of NH_3 over Cd^{2+} leads to the complete dissolution of $Cd(OH)_2$ and formation of cadmium ammonia complexes. However, we failed to deposit a solid, clear and uniform CdS films in this case.

The phase composition of the synthesized samples was determined by the X-ray diffraction analysis (Fig. 2). We found that the films are two-phase in all cases and consist of CdS compound in cubic (structural type ZnS, sphalerite) and hexagonal (structural type ZnO, wurtzite) modifications. The parameters of the CdS unit cells were as follows: a=0.5823(4) nm of cubic and a=0.4126(1) nm, c=0.6812(4) nm of hexagonal modification.

The results of the investigation of the surface morphology of CdS films are shown in Figs. 3 and 4. A series of microphotographs indicates that CdS films deposited at small amounts of $Na_3C_6H_5O_7$ (0.005–0.01 M) reveal a large amount of precipitate and defects on their surface. There is a deviation from stoichiometric composition as follows from the microanalysis results (Fig. 5). The CdS film was solid, clear and uniform over the whole area with a small number of surface defects at $C(Na_3C_6H_5O_7)$=0.1 M. At this concentration of sodium citrate, the investigation of the effect of deposition duration was carried out. It can be seen that CdS films have the

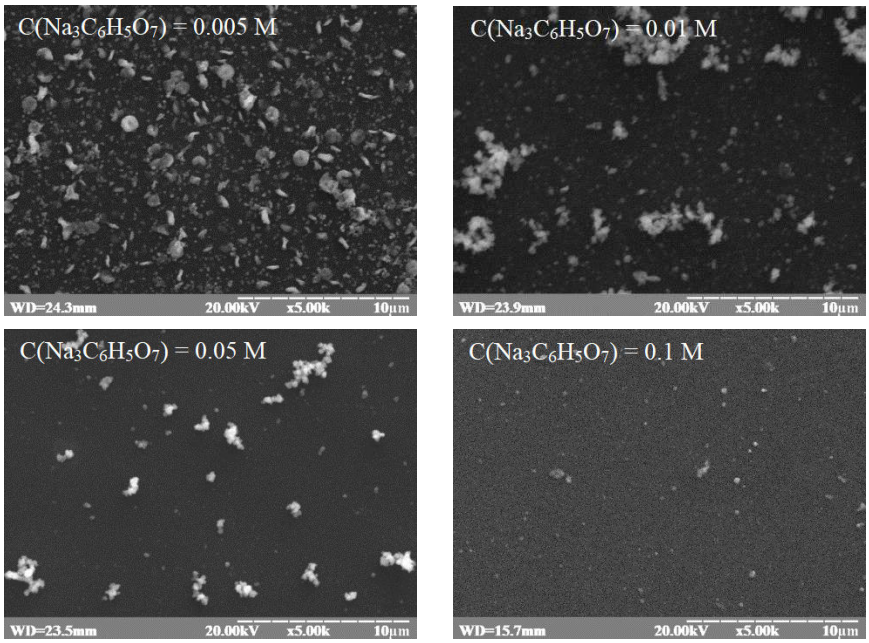

Fig. 3. Surface morphology of CdS films obtained at 60 min and different concentrations of sodium citrate

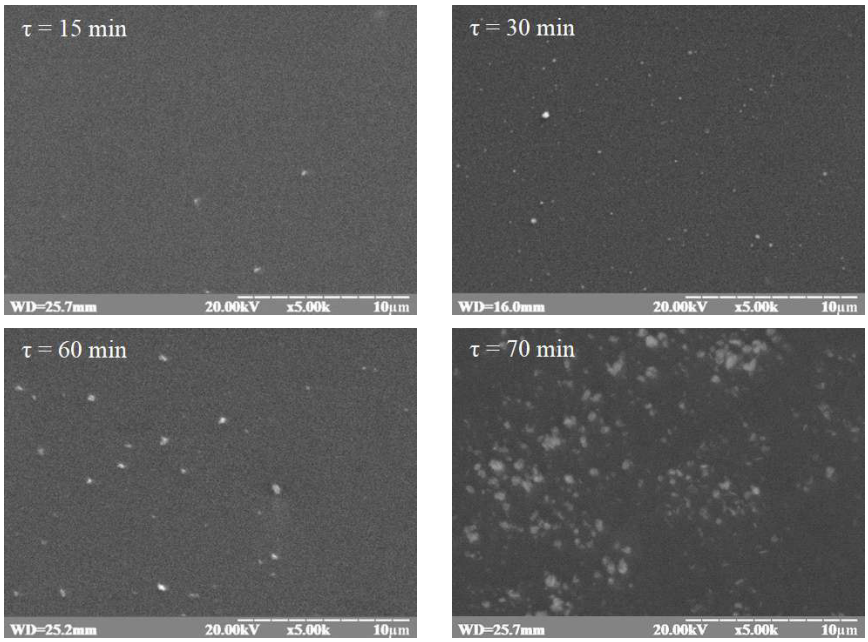

Fig. 4. Surface morphology of CdS films obtained at $C(Na_3C_6H_5O_7)$=0.1 M and different deposition duration

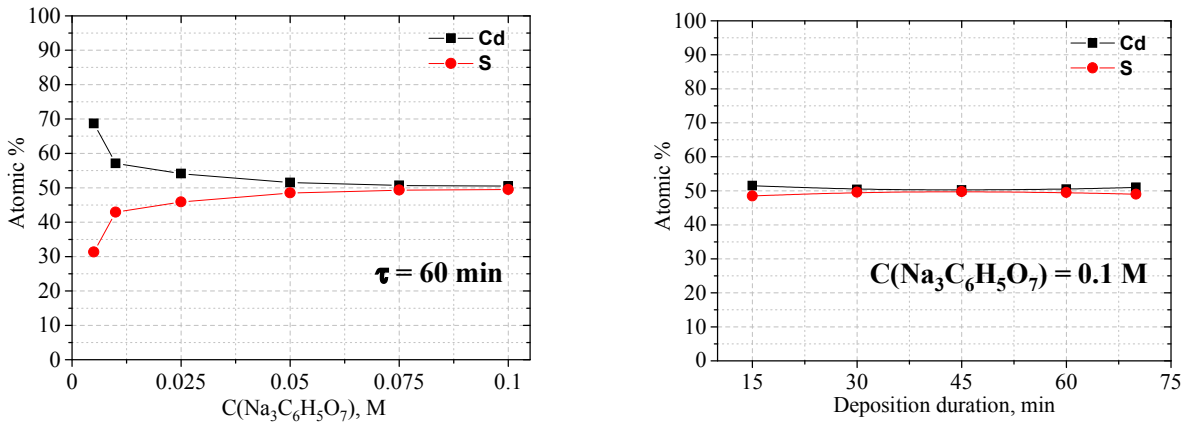

Fig. 5. The atomic composition of CdS films prepared at different concentrations of sodium citrate (left) and different deposition duration (right)

same good quality in 15–60 min region of deposition duration. At longer duration, the coating begins to adsorb the particles of CdS precipitate from the solution. The atomic composition of CdS films is practically stoichiometric with a slight excess of cadmium atoms in whole investigated region of deposition duration.

According to the results of the measurement of CdS films thickness (d), d values are below the minimum measured detection limit (<10 nm) during first 5–10 min of deposition (Fig. 6). The thickness increases from 12 to 42 nm at 15–30 min of deposition. The growth rate is the highest in this interval. The growth rate becomes lower at 35–70 min of deposition and the thickness increases from 45 to 64 nm.

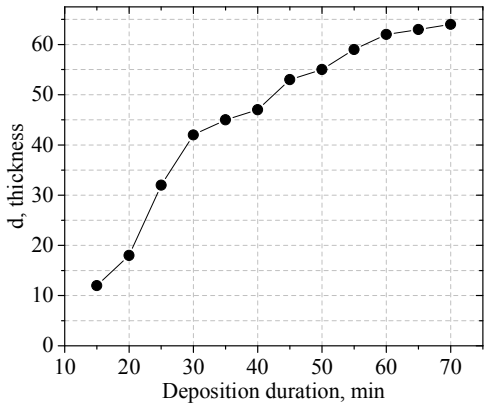

Fig. 6. Thickness of CdS films prepared at different deposition duration

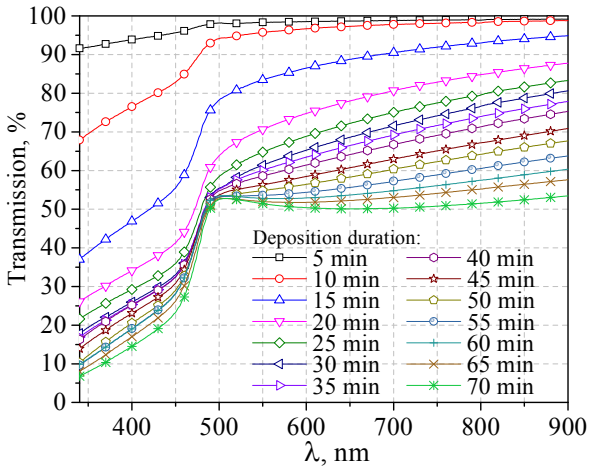

Fig. 7. Spectral dependences of optical transmission of CdS films obtained at different deposition duration

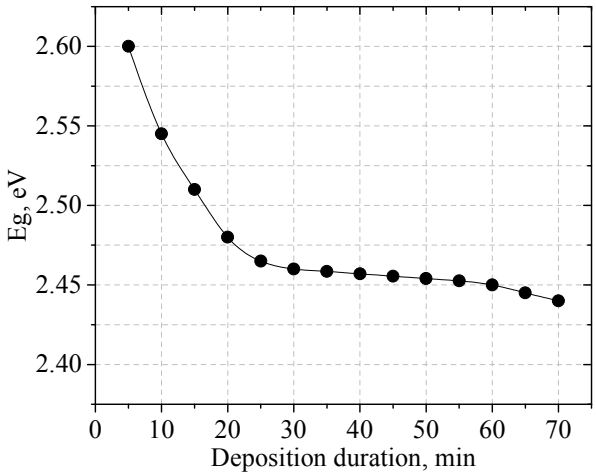

Fig. 8. Optical band gap of CdS films obtained at different deposition duration

The optical transmission spectra T(λ) of CdS films obtained at different deposition durations are shown in Fig. 7. The minimum light transmission (T_{min}) at the investigated range of wavelength is observed at 340 nm. An increase in the light transmission can be seen at greater wavelengths. The maximum light transmission (T_{max}) at investigated range of wavelengths located close to 900 nm. In the region of deposition duration of 5–70 min, the values of T_{min} and T_{max} decrease from ~92% to 7% and from ~99% to 53%, respectively, as a result of increasing the thickness of CdS films. The optical band gap (Fig. 8) numerically decreases from 2.60 to 2.44 eV with increasing the synthesis duration. These values are close to those described elsewhere [3,12]. The change of E_g can be explained by decreasing the quantum-size effect with increasing the thickness of CdS films.

The formation and further decomposition of an intermediate complex was earlier mentioned as one of possible way of the chemism of CdS formation [4]. The modeling and calculation of geometrical parameters and formation enthalpies were performed (in the conditions of water solution). The geometry of the starting complex of cadmium with citrate was taken from [13]. According to the results of

Table 2

Enthalpy values ($\Delta_f H$) and interatomic distances at modeled stages of CdS films synthesis in water solution

Stage	1	2	3	4	5	6
$\Delta_f H$, kJ/mol	–2866.63	–3226.74	–3266.53	–3250.09	–3221.43	–2934.53
A(N)–B(N)	Distance, nm					
Cd(14)–O(9)	0.2206	0.2285	0.2219	0.2197	0.2168	0.516
Cd(14)–O(12)	0.2233	0.2292	0.2266	0.2222	0.2175	0.5441
Cd(14)–O(13)	0.2351	0.2435	0.2471	0.2561	0.2356	0.478
Cd(14)–O(28)	0.4000	0.2033	0.2051	0.9943	1.0057	0.9565
Cd(14)–O(30)	0.4000	0.2033	0.2028	0.2011	1.1472	1.0960
Cd(14)–S(15)	0.8000	0.4000	0.4000	0.2532	0.2272	0.2120
S(15)–C(16)	0.1744	0.1744	0.1750	0.1822	0.7165	0.7165
C(16)–N(17)	0.1353	0.1356	0.1338	0.1382	0.1347	0.1347
C(16)–N(18)	0.1348	0.1352	0.1354	0.1291	0.1166	0.1166
O(28)–H(29)	0.0973	0.096	0.0958	0.0966	0.0963	0.0963
O(30)–H(31)	0.0891	0.0959	0.0961	0.0961	0.0963	0.0963
N(17)–H(24)	0.1013	0.1012	0.1092	0.1012	0.1029	0.1025
N(17)–H(25)	0.1016	0.1023	0.1011	0.1011	0.1026	0.1024
N(18)–H(26)	0.2206	0.2285	0.2219	0.2197	0.2168	0.5160
N(18)–H(27)	0.2233	0.2292	0.2266	0.2222	0.2175	0.5441
O(28)–H(24)	0.2351	0.2435	0.2471	0.2561	0.2356	0.4780
O(30)–H(25)	0.4000	0.2033	0.2051	0.9943	1.0057	0.9565

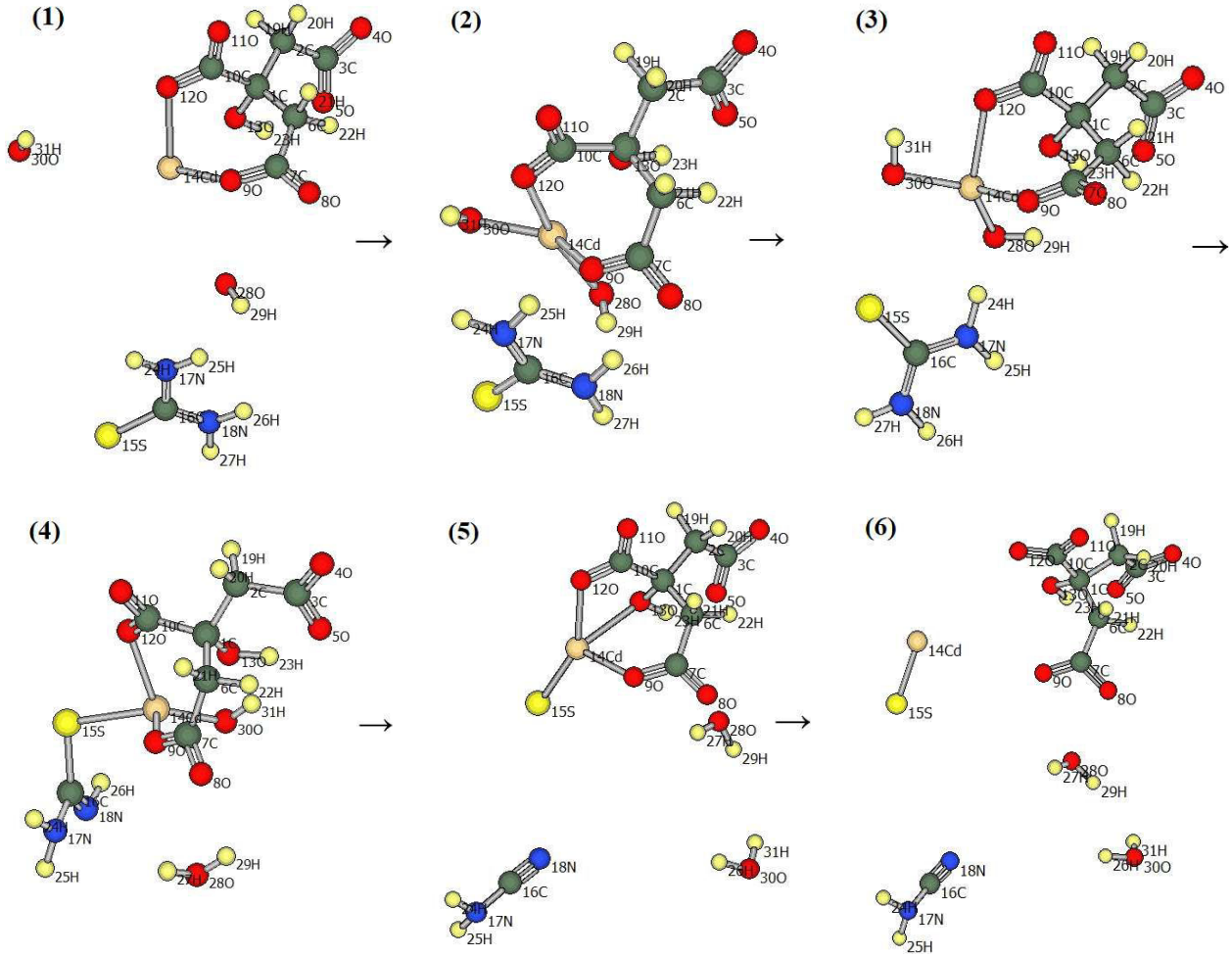

Fig. 9. The simulated stages (1–6) of CdS synthesis

calculations (Fig. 9, Table 2), it was found that the process passes through six stages.

At stages 1 and 2, two OH-groups approach cadmium and two-coordination Cd-complex $[Cd{\cdot\cdot}(C_6H_5O_7)]^-$ transforms into four-coordination intermediate complex $[(OH)_2{\cdot\cdot}Cd{\cdot\cdot}(C_6H_5O_7)]^{3-}$ (the distance of Cd(14)–O(28) and Cd(14)–O(30) decreases from 0.4000 nm to 0.2033 nm):

$$[Cd{\cdot\cdot}(C_6H_5O_7)]^- + 2OH^- \rightarrow [(OH)_2{\cdot\cdot}Cd{\cdot\cdot}(C_6H_5O_7)]^{3-}.$$

Here, the formation enthalpy (Δ_fH) decreases which means that the process is energetically profitable. Then, at stages 3 and 4, the distance between sulfur atom of thiourea and cadmium atom of intermediate complex (Cd(14)–S(15)) decreases from 0.4000 nm to 0.2532 nm. As a result, a transitional complex with thiourea ($[N_2H_3CS{\cdot}Cd{\cdot}(OH){\cdot\cdot}(C_6H_5O_7)]$) appears ($\Delta_fH$ changes slightly):

$$[(OH)_2{\cdot\cdot}Cd{\cdot\cdot}(C_6H_5O_7)]^{3-} + (NH_2)_2CS \rightarrow [N_2H_3CS{\cdot}Cd{\cdot}(OH){\cdot\cdot}(C_6H_5O_7)]^{3-} + H_2O.$$

It is destroyed with the formation of cadmium sulfide, cyanamide, citrate ion and water at last stages 4–6:

$$[N_2H_3CS{\cdot}Cd{\cdot}(OH){\cdot\cdot}(C_6H_5O_7)]^{3-} \rightarrow$$

$$\rightarrow CdS\downarrow + CH_2N_2 + C_6H_5O_7^{3-} + H_2O.$$

The interatomic distances of former thiourea atoms S(15)–C(16) and N(18)–H(26) increases from 0.1822 nm to 0.7165 nm and from 0.2197 nm to 0.5160 nm, respectively. When CdS is separated, the distances Cd(14)–S(15) decreases to 0.2110 nm. The Δ_fH increases at final stage, this indicates that supplying some energy into the system is required. The structure of citrate ligand did not change in the course of 1–6 stages.

Conclusions

In this work, an attempt was made to comprehensively consider the synthesis of cadmium sulfide films in order to develop general rules and approaches to control the process of their chemical bath deposition. It has been established that the use of $Na_3C_6H_5O_7$ as a complexing agent in synthesis results in the formation of the two-phase CdS films which are the mix of sphalerite and wurtzite. The effects of $Na_3C_6H_5O_7$ concentration and deposition duration on the morphological properties of CdS films and their atomic composition were shown. In practical plan, it is advisable to use sodium citrate of highest concentration in the investigated range at 60 min duration, because the films synthesized under such conditions are practically stoichiometric in composition, solid, clear and uniform. Their optical transmission decreases with increasing the deposition duration and it is possible to regulate the optical band gap in the range of 2.60 to 2.44 eV. The quantum-chemical modeling of possible chemism process of CdS synthesis showed that the cadmium sulfide is forming from cadmium citrate complex and thiourea via the formation of two intermediate complexes.

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СИНТЕЗ ТОНКИХ ПЛІВОК КАДМІЙ СУЛЬФІДУ З ВОДНОГО РОЗЧИНУ, ЩО МІСТИТЬ НАТРІЙ ЦИТРАТ

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Методом хімічного осадження з ванни одержано плівки кадмій сульфіду (CdS) на скляних підкладках з використанням водних розчинів кадмій хлориду, тіосечовини, натрій цитрату як комплексоутворюючого реагенту та аміаку як pH-регулятора. Було здійснено комплексні дослідження, які включають: теоретичний розрахунок граничних умов утворення кадмій сульфіду і кадмій гідроксиду в цитратно-аміачній системі, експериментальне дослідження складу, структури, оптики і морфології синтезованих напівпровідникових плівок CdS. Одержані плівки були двофазними та містили сполуку CdS в обох модифікаціях: сфалериту та вюрциту. Вони мають однорідну суцільну поверхню, практично стехіометричний склад та невеликий інтервал зміни оптичної ширини забороненої зони. Виконано квантово-хімічне моделювання можливого хімізму процесу синтезу CdS. За результатами розрахунків, сульфід кадмію утворюється з вихідного комплексу цитрату кадмію, пройшовши через утворення декількох проміжних комплексів. Аналіз отриманих експериментальних результатів дозволяє знайти зв'язок між умовами осадження CdS і властивостями одержаних напівпровідникових плівок, виявити переваги викори-

стання натрій цитрату як комплексоутворюючого реагенту і визначити доцільність його використання.

Ключові слова: кадмій сульфід, напівпровідникові плівки, хімічне осадження, оптичні властивості, аналіз морфології.

SYNTHESIS OF CADMIUM SULFIDE THIN FILMS FROM AN AQUEOUS SOLUTION CONTAINING SODIUM CITRATE

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The cadmium sulfide (CdS) films were prepared on glass substrates by chemical bath deposition method using aqueous solutions of cadmium chloride, thiourea, sodium citrate (complexing agent) and ammonia (pH regulator). A theoretical calculation of the boundary conditions of the formation of cadmium sulfide and cadmium hydroxide in the citrate-ammonia system was performed in this work. The composition, structure, optics and morphology of the synthesized CdS semiconductor films were experimentally investigated. The obtained films are two-phase and consist of CdS in both sphalerite and wurtzite modifications. They have a homogeneous solid surface, a practically stoichiometric composition and a narrow interval of the change of optical band gap. The quantum-chemical modeling of possible chemism of the CdS synthesis was performed. According to the results of the calculation, cadmium sulfide is formed from the initial cadmium citrate complex via the formation of several intermediate complexes. An analysis of the obtained experimental results allows finding the relationship between the deposition conditions and properties of the prepared semiconductor films, revealing the advantages of the use of sodium citrate as a complexing agent and determining the expediency of its application.

Keywords: cadmium sulfide; semiconductor film; chemical deposition; optical properties; morphology analysis.

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