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MODELING OF CHEMICAL SURFACE DEPOSITION (CSD) OF CdS AND CdSe SEMICONDUCTOR THIN FILMS

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Abstract. A mathematical model of the chemical surface deposition process of CdS and CdSe thin films, which allows determining the concentration of reagents, as well as duration and temperature for CSD needed to obtain films of the set thickness was designed. The adequacy of model was tested by Fisher's criterion. The nomogram of dependence of cadmium ions content on the initial deposition parameters was built according to the results of experimental studies and approximated by mathematical dependence.

Keywords: thin semiconductor films, chemical surface deposition, mathematical model, deposition process.

1. Introduction

The constant increasing of energy consumption and rising energy prices are stimulating the search of new methods and materials for direct photoconversion of solar energy. Critical analysis of scientific and technical literature shows that only thin-film solar cells (SC) can compete with traditional energy sources. High cost of production of photosensitive film-based structures hinders their industrial introduction. Using the chemical surface deposition (CSD) method for obtaining $A^{II}B^{VI}$ semiconductor materials, in particular CdS and CdSe films from aqueous solutions of cadmium-containing salts will allow to solve the problem of SC value decrease.

The CSD method is differing from others by the possibility to obtain coating of large areas at low temperatures, minimal using of reagents, and, accordingly, minimal number of waste. Photosensitive structures based on cadmium sulfide and cadmium selenide films, obtained by this method, by their physical parameters fully meet the requirements for application in thin-film SC.

Development of method and scientifically-based approach to the construction of analytical models of CSD thin semiconductor films and creation of such models for chemical reactions that have different kinetics is an urgent task. Currently, there are solitary models for individual processes of creating film coatings in a limited range of deposition parameters [1, 2]. A scientifically-based method for constructing of chemical deposition models of thin films on the surface of substrate to create photosensitive heterostructures is absent.

The aim of this work is establishing an analytical dependence between outgoing, incoming and controlled CSD process parameters of CdS and CdSe thin films and confirmation of the adequacy of established mathematical expression by the available scientific and experimental data.

2. Experimental

The working solution contained cadmium chloride ($CdCl_2$), thiourea $CS(NH_2)_2$ and 14.28 M solution of the ammonium hydroxide NH_4OH for deposition of films of cadmium sulfide (CdS). The working solution which consisted of cadmium chloride $CdCl_2$ and sodium selenosulphate Na_2SeSO_3 was used for the deposition of cadmium selenide thin films (CdSe). The molar concentrations of starting components varied from 0.01 to 0.05 M for cadmium containing salt, from 0.1 to 0.4 M for sodium selenosulfate and from 0.5 to 1.5 M for the thiourea. The deposition time and the process temperature varied for different samples from 3 to 12 min and from 323 to 363 K, respectively. Only freshly prepared reagents were entered to the working solutions for CSD of CdS and CdSe thin films.

Cadmium chloride has been the source of Cd^{2+} ions, thiourea – S^{2-} ions and sodium selenosulphate – of Se^{2-} ions. Sodium selenosulphate was prepared by dissolving crushed selenium in aqueous solution of sodium sulfite (Na_2SO_3) at 333 K under constant stirring for 3 h. After the end of the reaction the solution was cooled and filtered.

Amount of cadmium was determined by inversion voltammetry method in the obtained films after their dissolving in hydrochloric acid [3]. The relative value of standard deviation of measurement error results had not exceeded 4 % or $(5 \pm 0.2)\ 10^{-7}$ mg.

The research of the film surface morphology was investigated by using the scanning electron microscope EVO-40XVP (Carl Zeiss, Germany) with INCA Energy 350 microanalysis system (Oxford Instruments, England).

The effect of concentration and nature of the starting materials, temperature and deposition time on the morphological and optical properties, structure and microstructure of CdS semiconductor films has been studied for the establishment of optimal parameters of cadmium sulfide semiconductor films synthesis [4].

3. Results and Discussion

A mathematical model of deposition process of cadmium sulfide and cadmium selenide films was designed based on the obtained experimental data for more effective conducting of the experiments and reducing the cost to their organization.

Selected factors are:

– x_1 - initial cadmium-containing salt concentration C_1, mol/l;

– x_2 – thiourea concentration (sodium selenosulphate) C_2, mol/l;

– x_3 – process temperature T, °C;

– x_4 – deposition time t, min.

The data of factor levels and variation intervals for CdS and CdSe films, respectively, are in Tables 1 and 2. The planning matrix FFE 34 (full factorial experiment) with taking into account the effect of interactions factors was composed for maximum detection of factors influence on response function. Since there are four factors on 3 levels and therefore 81 experiments need to be conducted, it was advisable to build the central compositional rotatable plan (CCRP) of the 2nd order (not shown here), where the content of cadmium ions y in obtained thin films was the response function.

The experiments were randomized in time and every experiment (according to CCRP 31 were held) was repeated twice. The processing of measurements results was carried out by known methods of mathematical statistics which were reduced to scientific researches. The evaluation of experiments reproducibility confined to determination of the experiments reproducibility dispersion. Fisher's criterion (F) was used to verify the homogeneity of dispersions. Cochren's criterion (G) was used to confirm the homogeneity of dispersion. $G_{tabl} = 0.2113$ for the significance level of 0.05 is accepted from the corresponding table (not shown here) for the number of freedom degrees $f = n - 1 = 3$ and the number of experiments $N = 31$. Since the tabular value of Cochren's criterion is greater than the experimental one $0.0574 < 0.2113$ (for CdS films) and $0.1387 < 0.2113$ (for CdSe films) the homogeneity of dispersion is confirmed.

The regression coefficients are possible to determine because the dispersion uniformity was confirmed. The regression coefficients indicate how strong is the effect of factor on optimization parameter and how changing of factor will affect the change of response functions. The regression equation was written down after calculating regression coefficients (1 – for CdS films and 2 – for CdSe films):

$$y = 2.628 + 0.795 \cdot C_1 - 0.264 \cdot C_2 + 0.507 \cdot T + 0.381 \cdot t - 0.175 \cdot C_1 \cdot C_2 - 0.231 \cdot C_1 \cdot T + 0.212 \cdot \\ \cdot C_1 \cdot t - 0.358 \cdot C_2 \cdot T - 0.068 \cdot C_2 \cdot t - 0.358 \cdot T \cdot t + 0.114 \cdot C_1^2 + 0.062 \cdot C_2^2 - 0.090 \cdot T^2 + 0.031 \cdot t^2 \quad (1)$$

$$y = 3.597 + 0.245 \cdot C_1 - 0.044 \cdot C_2 + 0.872 \cdot T + 0.492 \cdot t - 0.049 \cdot C_1 \cdot C_2 - 0.231 \cdot C_1 \cdot T + 0.115 \cdot \\ \cdot C_1 \cdot t + 0.077 \cdot C_2 \cdot T + 0.037 \cdot C_2 \cdot t - 0.142 \cdot T \cdot t + 2.512 \cdot C_1^2 + 2.424 \cdot C_2^2 + 2.152 \cdot T^2 + 2.241 \cdot t^2 \quad (2)$$

Table 1

Factor levels and varying interval

Factor	Factor levels					Varying interval
	-2	-1	0	+1	+2	
x_1	0.01	0.02	0.03	0.04	0.05	0.01
x_2	0.50	0.75	1.00	1.25	1.50	0.25
x_3	50	60	70	80	90	10
x_4	1	2	3	4	5	1

Table 2

Factor levels and varying intervals

Factor	Factor levels					Varying interval
	-2	-1	0	+1	+2	
x_1	0.01	0.02	0.03	0.04	0.05	0.01
x_2	0.1	0.2	0.3	0.4	0.5	0.1
x_3	50	60	70	80	90	10
x_4	3	4	5	6	7	1

Since it was established that all factors are significant, it is possible to build the nomogram to obtain an empirical formula. Based on the results of experimental studies the nomogram of response function y dependence on the initial salt C_1 and thiourea C_2 concentration, process temperature T, and deposition time t is built and shown in Fig. 1.

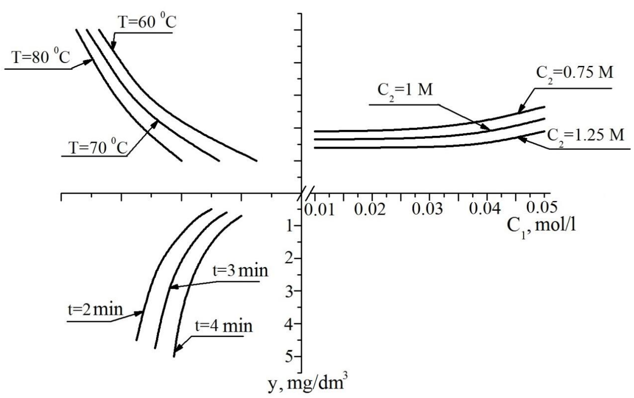


Fig. 1. Nomogram of response function y dependence on the initial salt C_1 and thiourea C_2 concentration, process temperature T (in Celsius degree) and deposition time t

The analysis of cadmium sulfide films CSD process nomogram allows us to make the following conclusions:

– increasing concentration of initial cadmium-containing salt from 0.01 to 0.035 M insignificantly affects the increasing content of cadmium ions. However, a significant effect on the value of cadmium ions content is observed on the area from 0.035 to 0.05 M;

– increasing process temperature from 323 to 343 K leads to a significant growth of the content of cadmium ions. Further increase of temperature practically does not change the content of cadmium ions;

– change of thiourea concentration in the range of 0.75–1.25 M insignificantly affects the content of cadmium ions;

– increase of the process duration leads to the growth of cadmium ions content.

The mathematical expression for calculation of content of cadmium ions is derived from the nomogram *via* the applied mathematics program:

$$
\begin{aligned}
y = {} & (9.00 - 0.91 \cdot t) + (-2.13 + 0.01 \cdot t) \cdot [(-23.76 + 0.36 \cdot T) + (13.43 - 0.13 \cdot T) \cdot \{(2.82 - 0.97 \cdot C_2) + \\
& + (-24.98 - 0.54 \cdot C_2) \cdot C_1 + (882.14 - 214.29 \cdot C_2) \cdot C_1^2\} + (-1.39 + 0.01 \cdot T) \cdot \{(2.82 - 0.97 \cdot C_2) + \\
& + (-24.98 - 0.54 \cdot C_2) \cdot C_1 + (882.14 - 214.29 \cdot C_2) \cdot C_1^2\}^2] + (0.1 + 0.03 \cdot t) \cdot [(-23.76 + 0.36 \cdot T) + \\
& + (13.43 - 0.13 \cdot T) \cdot \{(2.82 - 0.97 \cdot C_2) + (-24.98 - 0.54 \cdot C_2) \cdot C_1 + (882.14 - 214.29 \cdot C_2) \cdot C_1^2\} + \\
& + (-1.39 + 0.01 \cdot T) \cdot \{(2.82 - 0.97 \cdot C_2) + (-24.98 - 0.54 \cdot C_2) \cdot C_1 + (882.14 - 214.29 \cdot C_2) \cdot C_1^2\}^2]^2
\end{aligned}
$$

The optimum conditions, which were confirmed experimentally, were selected based on the suggested mathematical model and CdS and CdSe films were deposited from different cadmium-containing salts.

It was established that the optimum conditions, selected based on the model and confirmed according to the held experiments under which films with the highest cadmium content were produced, are:

– concentration of initial cadmium-containing salt – 0.01 mol/l;

– thiourea concentration – 1 mol/l;

– sodium selenosulphate concentration – 0.1 mol/l;

– process temperature – 343 K;

– deposition time – 3 min.

The confirmation of adequacy of the established mathematical expression is the fact that the content of cadmium in CdS films obtained at established optimal conditions differed from the calculated values by no more than 10 % (Fig. 2).

For CdSe films (Fig. 3) the difference between experimental and calculated values of content of cadmium is greater in CdSe films. This difference can be explained by differences in the deposition mechanisms of cadmium sulfide and cadmium selenide films.

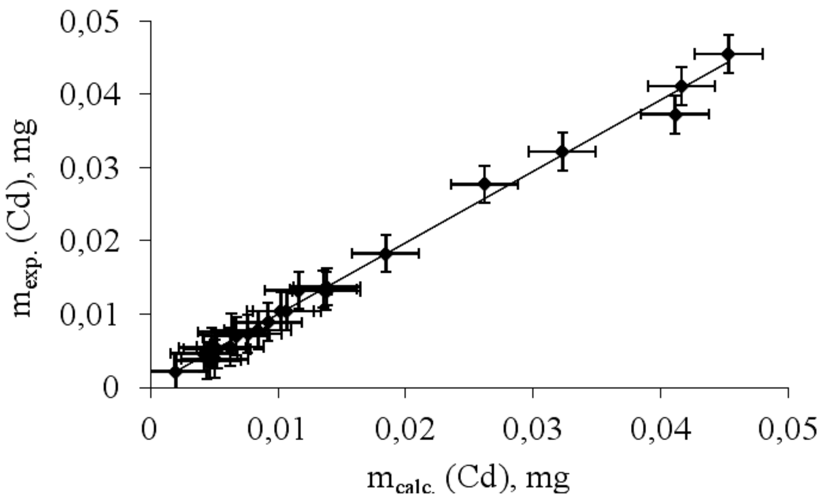


Fig. 2. The comparison of cadmium mass in CdS films obtained experimentally and calculated by a mathematical model

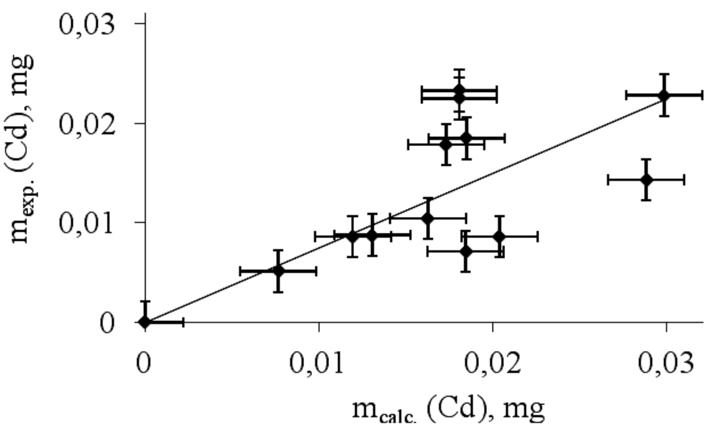


Fig. 3. The comparison of cadmium mass in CdSe films obtained experimentally and calculated by a mathematical model

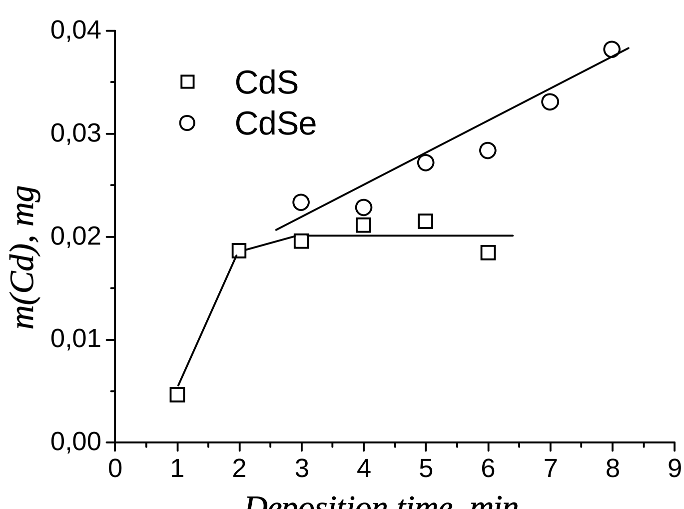
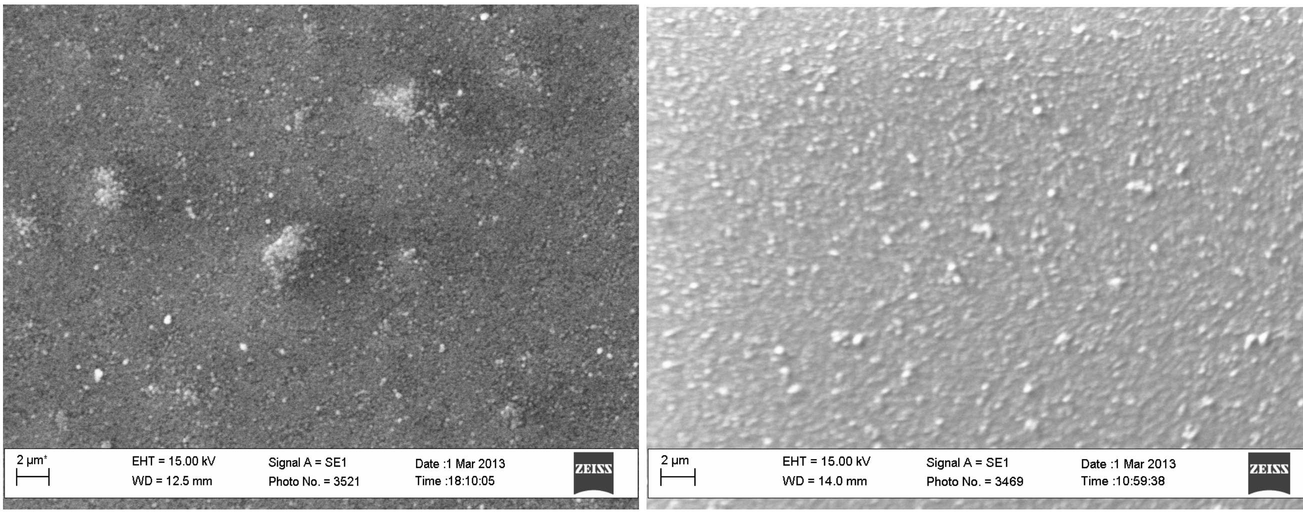


Fig. 4. Dependence of the mass of cadmium in CdS and CdSe films on the deposition time



a) b)

Fig. 5. Surface morphology of CdS (a) and CdSe (b) films. Magnification of 3000x. $C(CdCl_2)$ = 0.01 M, $C(CS(NH_2)_2)$ = 1 M, $C(Na_2SeSO_3)$ = 0.1 M; T = 343 K; deposition time (4x3) min; accelerating voltage of 15 kV

The films deposition occurs by heterogeneous nucleation of compound on the substrate surface at heat transfer to working solution by using CSD. The deposition of CdS thin films from aqueous solutions in alkaline medium passes through the stage of formation of tetraamine cadmium $[Cd(NH_3)_4]^{2+}$ complex ion [6], and CdSe – of selenosulphates complex anion and Cd^{2+} $[Cd(SeSO_3)_2]^{2-}$ [5, 7].

CdSe films would be formed sooner given the much smaller values of the solubility product of cadmium selenide compared with cadmium sulfide (SP(CdSe) = $(5\cdot10^{-35})$–$(1.1\cdot10^{-33})$, SP(CdS) = $(6.3\cdot10^{-29})$––$(6.5\cdot10^{-28})$). Cadmium sulfide films in the conditions of CSD were formed from the first minute, whereas at the deposition of cadmium selenide films considerable conspicuous (3 min) induction period is observed (Fig. 4).This difference testifies that the decomposition of $[Cd(NH_3)_4]^{2+}$ and $[Cd(SeSO_3)_2]^{2-}$ complex ions in alkaline medium are the limiting stages of CdS and CdSe films deposition, respectively. It was established by the authors [8] that the rate constant of the decomposition reaction of $[Cd(NH_3)_4]^{2+}$ ion ($k = 3.1\cdot10^{10}$ $M^{-1}s^{-1}$) has by order higher value than the constant of $[SeSO_3]^{2-}$ decomposition ($k = 2.3\cdot10^{9}$ $M^{-1}s^{-1}$).

Despite the mentioned differences solid strong CdS and CdSe films with the specular surface and with good adhesion to the substrate were deposited in the selected conditions on the basis of a mathematical model (Fig. 5).

The number of particles on the surface for CdS films is in the range of 10^6 cm^{-2}, and for CdSe films – 10^8 cm^{-2}. For comparison, most preferred results for the number of particles on the surface are 10^5 cm^{-2}, while for chemical bath deposition (CBD) – 10^8 cm^{-2} [9].

Thus, we can conclude that cadmium sulfide and cadmium selenide thin films which by their physical parameters meet the requirements for using in thin film solar cells were deposited based on the suggested mathematical model. The application of the proposed model for deposition of CdS thin films allows with high accuracy to choose CSD conditions for deposition of coatings of a given thickness. In the case of CdSe, the mathematical model should be improved taking into account the differences of decomposition reactions parameters of selenosulphate complex anion $[Cd(SeSO_3)_2]^{2-}$and Cd^{2+} in alkaline medium.

4. Conclusions

The analytical dependencies between outgoing, incoming and controlled CSD process parameters of CdS and CdSe thin films were established. Optimal conditions based on the mathematical model were selected and CdS thin films which by theirs parameters meet the requirements for using in thin film solar cells were deposited. The necessity to improve the mathematical expression for predicting the deposition process of cadmium selenide thin films taking into account the differences of decomposition reactions parameters of the selenosulphates complex anion with cadmium in alkaline medium was established.

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МОДЕЛЮВАННЯ І ОПТИМІЗАЦІЯ УМОВ ХІМІЧНОГО ПОВЕРХНЕВОГО ОСАДЖЕННЯ (ХПО) НАПІВПРОВІДНИКОВИХ ТОНКИХ ПЛІВОК CdS та CdSe

Анотація. *Розроблена математична модель процесу хімічного поверхневого осадження тонких плівок CdS та CdSe, яка дає можливість визначити концентрації реагентів, тривалість та температуру ХПО, необхідні для одержання плівок заданої товщини. Адекватність моделі перевірено за критерієм Фішера. За результатами експериментальних досліджень побудована номограма залежності вмісту йонів кадмію від вихідних параметрів осадження, яка апроксимована математичною залежністю.*

Ключові слова: *тонкі напівпровідникові плівки, хімічне поверхневе осадження, математична модель процесу осадження.*