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Mathematical approaches to a method of semiconductor materials films synthesis type $A^{II}B^{VI}$ for photosensitive structures used in alternative energy

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Abstract: The scientific direction of the synthesis of CdS and CdSe thin films by the method of chemical surface deposition (CSD) using aqueous solutions of cadmium-containing salts: chloride, nitrate, sulfate, acetate, iodide has been developed. A mathematical model of the CSD process of CdS and CdSe thin films was developed to improve the efficiency of experiments and reduce costs. The model makes it possible to determine the concentration of reagents, the duration, and the CSD temperature, which are necessary to obtain films of a specified thickness. The optimization of chemical deposition parameters of film-type semiconductor materials has been carried out. Based on the mathematical model, the optimal synthesis conditions were the next: concentration of cadmium-source salt – 0.01 mol/L, chalcogenizer – 1.0 mol/L or 0.1 mol/L in the chase of thiourea or sodium selenosulfate, respectively; temperature – 70 °C and duration of 3 min. The mathematical dependence of the experimental studies results of the metal ions content in thin-film solar cells for the effective direct conversion of solar radiation into electrical energy taking into account errors was proposed.

Keywords: thin films; chemical surface deposition; solar cells.

INTRODUCTION

Now in the public consciousness, there is a growing conviction that the energy of the future should be based on the large-scale use of solar energy, and in its various manifestations. The bet on solar energy should be seen not only as a win-win but in the long term and as no choice for humanity. We will consider the possibilities of converting solar energy into electrical energy using semiconductor solar photocells in retrospective and prospective terms. These devices appear to be quite mature scientifically and technologically today to be regarded as the technical

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basis for the large-scale solar power of the future. Photovoltaic converters of solar energy occupy a special place among alternative and renewable energy sources.

Solar PV cells are a very real technically and cost-effective alternative to fossil fuels in several applications. The solar cell can directly convert solar radiation into electricity without the use of any moving mechanisms. Due to this, the service life of solar generators is quite long. Photovoltaic systems have proven themselves well since the beginning of the industrial application of photovoltaic cells.

Improving the photoconversion efficiency by increasing the short-circuit current in solar cells with a CdS or CdSe buffer layer requires a decrease in losses for optical absorption of photons with energies hν <2.4 eV, which can be achieved by minimizing the thickness of cadmium sulfide and cadmium selenide films to optimal sizes. Therefore, studies of the deposition process of CdS and CdSe thin films with the given photoelectric properties for the creation based on them of thin-film solar cells are of considerable practical interest.

The search for new approaches to obtaining films of $A^{II}B^{VI}$ semiconductor materials, in particular CdS and CdSe films, will solve the problems of reducing the cost of photosensitive elements, a comprehensive study of the electrophysical properties of film-type semiconductor materials and structures based on them, the attracting of new methods for their implementation. The prospect of this direction is justified by the fact that, despite numerous studies, semiconductor photosensitive structures based on cadmium sulfide and cadmium selenide thin films are widely used in thin-film solar cells for efficient direct conversion of solar radiation into electrical energy [1-2]. The industrial introduction of such elements and the use of solar modules in alternative energy is hindered by the high cost of their manufacture, and, accordingly, the high cost of electricity produced by them. The manufacturing cost can be significantly reduced if the method for obtaining thin films is simple and will not require the use of high temperatures and expensive initial materials.

The operation of thin-film elements is based on a Cd (S, Se)/CdTe or Cd (S, Se)/Si heterojunction, and their parameters and technical characteristics are determined by the properties of thin films and the conditions for making the heterojunctions. Therefore, the development of the synthesis basis of CdS and CdSe continuous semiconductor thin films from aqueous solutions using a simple and reproducible method that must satisfy the economic and environmental aspects of production and must ensure high quality of the material is an important and actual scientific problem[3]. The use of mathematical modelling for the decrease of the film manufacturing cost and increase of its production amount was not observed in the scientific research in this field, which can open a new approach to economical, and environmentally friendlier semiconductor synthesis in terms of decreasing the amount of by-products formation and the increase of the effectiveness of reactants conversion.

To obtain a high-quality mathematical model, it is essential to gather a substantial amount of experimental data related to the nature of the initial agents, concentration, synthesis temperature and duration, as well as film thickness.

To acquire this data, the following steps are necessary:

1. Choose the synthesis technique, initial substances, and synthesis conditions.
2. Produce several thin film samples.
3. Determine their thickness, optical, and morphological properties.
4. Establish relationships between these properties.

Chemical surface deposition (CSD)

To achieve the goals of this research, first of all, it was necessary to choose the film synthesis technique because the number of factors which should be used for the mathematical modelling and the quality of the film directly depends on the process which lay in its base. For this reason, we decided to use the chemical surface deposition technique since it requires the minimum amount of reactants, and this method is ideal for the production of thin films over large areas at temperatures <100 °C, which is one of the main requirements for the mass use of solar energy. The technology of chemical deposition of semiconductor films consists of the deposition of a solution containing metal ions and a source of sulfur or selenium ions onto a substrate. The deposition of CdS thin films from aqueous solutions is a reaction between cadmium salts and thiourea in an alkaline medium [4-5]. To obtain high-quality cadmium coatings, it is necessary to use well-water-soluble cadmium sources, which will be cheap and would not provide any additions, which may cause the formation of other undesirable by-products. For this purpose, it perfectly fits some simple cadmium salts. Preferably, the most used are $CdSO_4$, CdI_2, $Cd(NO_3)_2$, $Cd(CH_3COO)_2$, and $CdCl_2$. Thiourea is used as a sulfur-containing agent in sulfide deposition reactions since it has a high affinity for metal cations and decomposes at low temperatures. The deposition process can be described by two mechanisms: homogeneous and heterogeneous.[6]

The homogeneous mechanism presupposes the formation of a coating of colloidal CdS particles, which are formed in solution and consist of several stages:

1. Dissociation of ammonium hydroxide:

$$\mathrm{NH_4^+ + OH^- \rightarrow NH_3 + H_2O} \tag{1}$$

In an alkaline medium due to the interaction of ions Cd^{2+} with ions OH^- is the possible formation of an undesirable product - $Cd(OH)_2$ [4-5]:

$$\mathrm{Cd^{(2+)} + OH^- \rightarrow Cd(OH)_2 \downarrow} \tag{2}$$

2. Hydrolysis of thiourea $(NH_2)_2CS$ with the formation of sulfide ions (S^{2-}):

$$\mathrm{(NH_2)_2CS + H_2O \rightarrow HS^- + H^+ + (NH_2)_2CO} \tag{3}$$

$$\mathrm{HS^- + OH^- \rightarrow S^{2-} + H_2O} \tag{4}$$

3. Formation of the final product:

$$Cd^{2+} + S^{2-} \rightarrow CdS\downarrow \quad (5)$$

According to the heterogeneous mechanism of CdS thin films deposition from aqueous solutions passes through the stage of cadmium tetraamine $[Cd(NH_3)_4]^{2+}$ complex ion formation, which reduces the overall reaction rate and prevents the formation of $Cd(OH)_2$ [7]. The formed cadmium tetraamine ion interacts with sulfide ions, which are formed by hydrolysis of thiourea (equations (3) and (4)):

$$Cd^{2+} + 4NH_4OH \rightarrow [Cd(NH_3)_4]^{2+} + 4H_2O \quad (6)$$

$$[Cd(NH_3)_4]^{2+} + S^{2-} \rightarrow CdS\downarrow + 4NH_3 \quad (7)$$

In general:

$$[Cd(NH_3)_4]^{2+} + (NH_2)_2CS + OH^{-} \rightarrow CdS\downarrow + 4NH_3 + H^{+} + (NH_2)_2CO \quad (8)$$

The deposition of sulfide films from thiourea coordination compounds has several chemical features.

Depending on the salt nature and the composition of the solution different coordination forms may dominate, moreover together with the thiourea molecules the anions Cl^-, Br^-, I^- may enter the complex inner sphere under certain conditions SO_4^{2-}. Thus, the nearest environment of cadmium atoms can be sulfur, halogen, and oxygen atoms, moreover, during thermal destruction, some of the Cd-Hal or Cd-O bonds are stored and defects $Hal_S^{\bullet}$ and $O_S^{\bullet}$ are formed in the sulfide lattice.[8]

The orientation of thiourea complexes occurs on the active centers of its surface at the interaction with the substrate. Complex particles capable of interacting with the active centers of the substrate are the link that provides the binding of sulfide to the substrate. The nature of this interaction also determines the nature of film adhesion.

In the case of cadmium sulfide deposition on quartz or glass substrates, the active centers are silanol groups (≡Si–OH), which interact with halide or hydroxyl mixed complexes. As a result of this interaction, oxygen bridges of the Cd–O–Si type are formed.[9] This explains the good adhesion of cadmium sulfide films obtained from thiourea coordination compounds to glass substrates.

CSD technology allows to obtain of thin films by using the sample surface as a heat source. The surface tension of the solution ensures that the volume of liquid used is minimized. The combination of the heat delivery method to the surface and a small volume of the solution leads to the high utilization of cadmium and its compounds.

Summarizing the above it can be argued that due to several disadvantages of the described methods for obtaining compounds of the $A^{II}B^{VI}$ group, the search for more efficient, cost-effective technologies is relevant. In this aspect, the CSD method of thin semiconductor films is of considerable interest. This is indicated by numerous publications and research studies conducted by us.

The process of chemical surface deposition was carried out at room temperature by dosed application of the working solution on a pre-prepared surface of an optically homogeneous glass plate (18×22 mm). The plates with the working solution were placed on a preliminarily thermostated surface to ensure uniform heating. The surface tension of the solution ensures that the volume of the reaction mixture is minimized and its retention on the substrate at the CSD method.

The film deposition occurs by heterogeneous nucleation of the compound on the substrate surface during heat transfer to the solution (Fig. 1). Heterogeneous nucleation is preferred over homogeneous fallout due to thermal stimulation of chemical activity on a warmer growth surface. As a result, we obtain a high proportion of cadmium from the solution in the film and depending on the substrate heteroepitaxial growth of the film. The heat outflow from the solution to the environment helps to maintain favorable conditions for the heterogeneous growth of the film over the period required for the film deposition. After heating the glass plate was taken away, and the surface was washed with a stream of distilled water and dried in air.

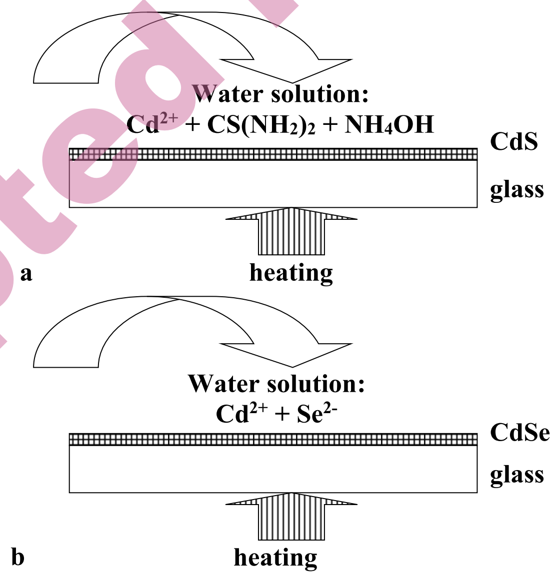

Fig. 1. The scheme of obtaining thin films (a – CdS; b – CdSe).

Freshly prepared aqueous solutions of cadmium salts were used to obtain CdS and CdSe thin films by CSD: $Cd(CH_3COO)_2$, $CdSO_4$, $CdCl_2$, $Cd(NO_3)_2$, CdI_2. The solutions composition and the corresponding concentrations are given in Table I and Table II.

TABLE I. Composition and solutions concentrations for CdS films

Salt	C(cadmium salts), mol/L	$C(CS(NH_2)_2)$, mol/L	$C(NH_4OH)$, mol/L	Temperature, °C
$Cd(CH_3COO)_2$ $CdCl_2$ CdI_2 $CdSO_4$ $Cd(NO_3)_2$	0.01-0.05	0.5-1.5	1.8	50.0-90.0

TABLE II. Composition and solutions concentrations for CdSe films

Salt	C(cadmium salts), mol/L	$C(Na_2SeSO_3)$, mol/L	Temperature, °C
$Cd(CH_3COO)_2$ $CdCl_2$ CdI_2 $CdSO_4$ $Cd(NO_3)_2$	0.01-0.05	0.1-0.4	50.0-90.0

CSD allows to obtain of films with structural, optical, and electrical parameters that are not inferior to films obtained by other methods. Also, CSD makes it possible to control film growth, maintain accurate process parameters, and dynamically change conditions to obtain homogeneous continuous films of a given thickness. This reduces the amount of waste and the volume of solutions containing cadmium ions eliminates mixing. The equipment used is affordable and does not require the use of high temperatures and pressures, which reduces energy consumption and simplifies and reduces the cost of technology.

EXPERIMENTAL

A mathematical model of the film's deposition process was developed based on the experiments for more efficient experiments and reduction of costs for its organization following existing techniques.[10-12]

Factors selected:

- x_1 - concentration of starting cadmium-containing salt, C_1, mol/L;
- x_2 - concentration of thiourea or sodium selenosulfate, C_2, mol/L;
- x_3 - process temperature, T, °C;
- x_4 - deposition time, t, min.

All chemicals used in the experiments were high-purity grade (Se, $Cd(CH_3COO)_2$, $CdSO_4$, $CdCl_2$, $Cd(NO_3)_2$, CdI_2, *Alfa Aesar GmbH*) and analytical grade (NH_4OH, $(NH_2)_2CS$, Na_2SO_3, *Sfera Sim LTD.*) or were freshly synthesized before the experiment (Na_2SeSO_3).

Table III gives data on the factor levels and variation intervals. A planning matrix for FFE 3^{10} (full factorial experiment) was compiled for maximum detection influence of factors on the response function taking into account the effect of factors interaction. Since four factors are at 3 levels and we need to carry out 81 experiments, it is advisable to build a central compositional rotatable plan of the 2nd order (CCRP) see Table IV. The response function is the content of cadmium ions in the experimentally obtained thin films samples - y.

TABLE III. Factors levels and variations intervals

The factor name	Coded designation	Factors levels -2	-1	0	+1	+2	Variations interval
C_1 - concentration of starting cadmium-containing salt, mol/L	x_1	0.01	0.02	0.03	0.04	0.05	0.01
C_2 – concentration of thiourea, mol/L	x_2	0.50	0.75	1.00	1.25	1.50	0.25
T – temperature, °C	x_3	50	60	70	80	90	10
t – time, min	x_4	1	2	3	4	5	1

TABLE IV. Central compositional rotatable plan of the 2nd order

№	x_0	x_1	x_2	x_3	x_4	x_1x_2	x_1x_3	x_1x_4	x_2x_3	x_2x_4	x_3x_4	x_1^2	x_2^2	x_3^2	x_4^2	y_1	y_2	y_{cp}
1	1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	1	1	0.5461	0.5457	0.5459
2	1	1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1.7991	1.7985	1.7988
3	1	-1	1	-1	-1	-1	1	1	-1	-1	1	1	1	1	1	1.3801	1.3807	1.3804
4	1	1	1	-1	-1	1	-1	-1	-1	-1	1	1	1	1	1	1.8431	1.8436	1.8434
5	1	-1	-1	1	-1	1	-1	1	-1	1	-1	1	1	1	1	2.9211	2.9217	2.9214
6	1	1	-1	1	-1	-1	1	-1	-1	1	-1	1	1	1	1	4.5695	4.5705	4.5700
7	1	-1	1	1	-1	-1	-1	1	1	-1	-1	1	1	1	1	2.4828	2.4836	2.4832
8	1	1	1	1	-1	1	1	-1	1	-1	-1	1	1	1	1	2.8713	2.8723	2.8718
9	1	-1	-1	-1	1	1	1	-1	1	-1	-1	1	1	1	1	1.6245	1.6239	1.6242
10	1	1	-1	-1	1	-1	-1	1	1	-1	-1	1	1	1	1	5.2207	5.2203	5.2205
11	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	1	1	1	2.5233	2.5238	2.5236
12	1	1	1	-1	1	1	-1	1	-1	1	-1	1	1	1	1	4.5049	4.5059	4.5054
13	1	-1	-1	1	1	1	-1	-1	-1	-1	1	1	1	1	1	4.3119	4.3129	4.3124
14	1	1	-1	1	1	-1	1	1	-1	-1	1	1	1	1	1	4.6616	4.6608	4.6612
15	1	-1	1	1	1	-1	-1	-1	1	1	1	1	1	1	1	2.6176	2.6184	2.6180
16	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3.8286	3.8294	3.8290
17	1	-2	0	0	0	0	0	0	0	0	0	4	0	0	0	0.7649	0.7639	0.7644
18	1	2	0	0	0	0	0	0	0	0	0	4	0	0	0	4.8556	4.8548	4.8552
19	1	0	-2	0	0	0	0	0	0	0	0	0	4	0	0	3.6848	3.6842	3.6845
20	1	0	2	0	0	0	0	0	0	0	0	0	4	0	0	2.3208	2.3212	2.3210
21	1	0	0	-2	0	0	0	0	0	0	0	0	0	4	0	1.1612	1.1604	1.1608
22	1	0	0	2	0	0	0	0	0	0	0	0	0	4	0	2.8301	2.8294	2.8298
23	1	0	0	0	-2	0	0	0	0	0	0	0	0	0	4	2.9131	2.9125	2.9128
24	1	0	0	0	2	0	0	0	0	0	0	0	0	0	4	2.0433	2.0443	2.0438
25	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.6346	2.6338	2.6342
26	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.6156	2.6146	2.6151
27	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.6065	2.6061	2.6063
28	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.6518	2.6528	2.6523
29	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.6159	2.6151	2.6155
30	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.6242	2.6248	2.6245
31	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.6471	2.6475	2.6473

The experiments were randomized in time, and each experiment, according to the planning matrix of Table IV, was repeated twice.

RESULTS AND DISCUSSION

The processing of the measurement results was carried out by the well-known methods of mathematical statistics brought to scientific research.[13-15] Each experiment was accompanied by the occurrence of errors, i.e. by the reproducibility errors. Each experiment was carried out several times to assess reproducibility, so a series of parallel experiments were organized. Evaluation of the experiments' reproducibility was reduced to determining the dispersion of experiments' reproducibility.

Also, randomization of experiments was carried out to eliminate systematic errors, when drawing up a plan of a matrix of the experiment. The experiments were carried out in a random sequence, which was established using a table of random numbers.

During the experiments, each experiment was carried out twice, under the same conditions, to be able to estimate the errors. During each experiment, the values of the averaged optimization parameters were obtained.

The deviation of the result of any experiments from the arithmetic mean indicates the variability of parallel experiments. A variance can be used to measure this variability:

$$s^2 = \frac{\sum_1^n (y_i - y_{cp})^2}{n-1}, \tag{9}$$

where $(n - 1)$ – the number of degrees of liberty, which is 1 less than the number of experiments.

The quadratic error is determined:

$$s = \sqrt{\frac{\sum_1^n (y_i - y_{cp})^2}{n-1}} \tag{10}$$

Fisher's criterion F was used to check the homogeneity of variances, which is equal to the ratio of the larger variance s^2_{max} to the smaller variance s^2_{min}:

$$F = \frac{s^2_{max}}{s^2_{min}}. \tag{11}$$

Further, the obtained value of F was compared with the tabular value of Fisher's criterion F_{tabl}. If the tabular value is less than the value obtained from the experiment, then this dispersion is inhomogeneous and additional verification of the measurement results is required.

For inhomogeneous dispersions, as well as for the certainty of the dispersion homogeneity, the Cochran criterion G was used.

The results of processing experimental data are presented in Table SI.

Fisher's criterion:

$$F = \frac{0.00000100}{0.00000016} = 6.25. \tag{12}$$

The value of the Fisher criterion for the significance level 0.05 was taken from the corresponding table: $F_{tabl} = 19$.

Comparing the obtained from the experiments and the tabular value of Fisher's criterion 6.25 <19 it is seen that the tabular value is greater than the experimental one. But to be sure, Cochran's criterion was used:

$$G = \frac{s^2_{max}}{\sum_1^N s_i^2 \frac{0.00000100}{0.00001743}}. \tag{13}$$

From the corresponding table for the number of degrees of freedom $f = n - 1 = 3$ and the number of experiments $N = 31$, $G_{tabl} = 0.2113$ is taken for a significance level of 0.05.

Since the tabular value of the Cochran criterion is greater than the experimental 0.0574 < 0.2113, the homogeneity of the dispersion is confirmed.

After checking for homogeneity, the variance is averaged and the following formula is used:

$$s^2(y) = \frac{\sum_1^N \sum_1^n (y_i - y_{cp})}{N(n-1)}. \tag{14}$$

Therefore, the reproducibility variance is equal:

$$s^2(y) = \frac{0.00001743}{31(4-1)} = 1.8742 \cdot 10^{-7}. \tag{15}$$

The reliability of the results of experimental measurements of the content of cadmium ions was checked for adequacy according to the corresponding Fisher and Cochran criteria outside the confidence interval $\alpha = 0.95$.

Since the homogeneity of the variance has been confirmed, it is possible to average the variance and use formula (9):

$$s^2(y) = \frac{\sum_1^N \sum_1^n (y_i - y_{cp})^2}{N(n-1)} = \frac{1.27 \cdot 10^{-11}}{31 \cdot (4-1)} = 1.36 \cdot 10^{-13} \tag{16}$$

Regression coefficients were determined by formulas:

$$b_0 = \frac{A}{n}\left[2\lambda^2(k+2)\sum_{u=1}^n y_u - 2\lambda c \sum_{i=1}^k \sum_{u=1}^n x_{iu}^2 y_u\right], \tag{17}$$

$$b_i = \frac{c}{n}\sum_{u=1}^n x_{iu} y_u \tag{18}$$

$$b_{ij} = \frac{c^2}{n\lambda}\sum_{u=1}^n x_{iu} x_{ju} y_u \tag{19}$$

$$b_u = \frac{A}{n}\left\{c^2[(k+2)\lambda - k]\sum_{u=1}^n x_{iu}^2 y_u + c^2(I - \lambda)\sum_{i=1}^k \sum_{u=1}^n x_{iu}^2 y_u - 2\lambda c \sum_{u=1}^n y_u\right\} \tag{20}$$

In these formulas, the following designations are accepted:

$c = \frac{n}{\sum_{u=1}^n x_{iu}^2}$; $\lambda = \frac{n 2^k}{\left(\sum_{u=1}^n x_{iu}\right)^2}$ - for a plan whose core is a full factorial experiment; $\lambda = \frac{n 2^{k-1}}{\left(\sum_{u=1}^n x_{iu}\right)^2}$ - for a plan whose core is semi-replicas from a full factorial experiment; $A = \frac{1}{2\lambda[(k+2)\lambda - k]}$.

As can be seen from the above formulas, the influence of the plan core structure on the values of the regression coefficients is taken into account by the value of λ. If formulas (17) - (20) calculate all the values that depend on the plan structure, they can be written as:

$$b_0 = \delta_0^{/} \sum_{u=1}^{n} y_u - \delta_0^{//} \sum_{u=1}^{n} \sum_{i=1}^{k} x_{iu}^2 y_u \quad (21)$$

$$b_i = \delta_i \sum_{u=1}^{n} x_{iu} y_u \quad (22)$$

$$b_{ij} = \delta_{ij} \sum_{u=1}^{n} x_{iu} x_{ju} y_u \quad (23)$$

$$b_{ll} = \delta_u^{/} \sum_{u=1}^{n} x_{iu}^2 y_u + \delta_{il}^{//} \sum_{i=1}^{k} \sum_{u=1}^{n} x_{iu}^2 y_u - \delta_{ll}^{///} \sum_{u=1}^{n} y_u \quad (24)$$

The values of δ included in formulas (21) - (24) can be taken from Table V. The data given in the tables provide everything for the construction of rotatable plans and minimize the calculations required to obtain the regression coefficients.[16]

TABLE V. Data for calculating regression coefficients in second-order rotatable planning

The plan core	b_0		b_i	b_{ij}	b_{ii}		
	$\delta_0^{/}$	$\delta_0^{//}$	δ_i	δ_{ij}	$\delta_{ii}^{/}$	$\delta_{ii}^{//}$	$\delta_{ii}^{///}$
2^2	0.200000	0.100000	0.125000	0.250000	0.125000	0.018750	0.100000
2^3	0.166338	0.056791	0.073224	0.125000	0.062500	0.006889	0.056791
2^4	0.142857	0.035714	0.041667	0.062500	0.031250	0.003720	0.035714
2^{4-1}	0.150091	0.034091	0.041667	0.062500	0.031250	0.002841	0.034091
2^5	0.099982	0.019392	0.023088	0.031346	0.015666	0.001523	0.019392
2^{6-1}	0.110749	0.018738	0.023087	0.031250	0.015625	0.001217	0.018738
2^6	0.066653	0.010553	0.012499	0.015833	0.007914	0.000681	0.010553
2^{7-1}	0.070312	0.009766	0.012500	0.015625	0.007812	0.000489	0.009766
2^7	0.047611	0.006428	0.006656	0.008089	0.004044	0.000418	0.006428

The following model is accepted:

$$y_i = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{14} x_1 x_4 + b_{23} x_2 x_3 + b_{24} x_2 x_4 + b_{34} x_3 x_4 + x_1^2 + x_2^2 + x_3^2 + x_4^2 \quad (25)$$

After calculating the regression coefficients, you can write the regression equation:

$$y = (9.00 - 0.91x_4) + (-2.13 + 0.01x_4)p + (0.10 + 0.03x_4)p^2 \quad (26)$$

where: $p = (-23.76 + 0.36x_3) + (13.43 - 0.13x_3)t + (-1.39 + 0.01x_3)t^2$; $t = (2.82 - 0.97x_2) + (-24.98 - 0.54x_2)x_1 + (882.14 - 214.29x_2)x_1^2$; x_1, x_2, x_3 and x_4 – coded designations from Table III.

The regression coefficients show how strongly the factor affects the optimization parameter and how a change in the factor will affect the change in the response function.

It is necessary to hold statistical estimates by obtaining a polynomial model. This procedure, described earlier, remains unchanged when experimenting with a rotatable plan. The difference is that the regression coefficients are determined with different variances, which are calculated using the following formulas:

$$s_{b_0}^2 = \frac{2A\lambda^2(k+2)}{n} s_y^2 \tag{27}$$

$$s_{b_i}^2 = \frac{c}{n} s_y^2 \tag{28}$$

$$s_{b_{ll}}^2 = \frac{A[(k+2)\lambda-(k-1)]c^2}{n} s_y^2 \tag{29}$$

$$s_{b_{il}}^2 = \frac{c^2}{n\lambda} s_y^2 \tag{30}$$

Formulas (27) - (30) can be rewritten as: $s_{b_0}^2 = \gamma_0 s_y^2$; $s_{b_{il}}^2 = \gamma_{il} s_y^2$; $s_{b_i}^2 = \gamma_i s_y^2$; $s_{b_{ij}}^2 = \gamma_{ij} s_y^2$.

The corresponding values of γ are summarized in Table VI.[16]

TABLE VI. Data for determining the variances of regression coefficients in rotatable planning of the second-order

The plan core	γ_0	γ_i	γ_{ij}	γ_{li}
2^2	0.2000	0.1250	0.2500	0.1250
2^3	0.1663	0.0732	0.1250	0.0625
2^4	0.1429	0.0417	0.0625	0.0312
2^{5-1}	0.1591	0.0417	0.0625	0.0312
2^5	0.1000	0.0231	0.03125	0.0157
2^{6-1}	0.1107	0.0231	0.03125	0.0156
2^6	0.0667	0.0125	0.0158	0.0079
2^{7-1}	0.0703	0.0125	0.0156	0.0078
2^7	0.0476	0.0067	0.0081	0.0040

Experimental error in rotatable planning can be determined by:

$$s_0^2 = \frac{\sum_{u=1}^{n_0}(y_{0_u} - \overline{y_0})^2}{n_0 - 1} \tag{31}$$

The numerator of expression (31) is the residual sum of squares in the center of the plan:

$$s_0 = \sum_{u=1}^{n_0}(y_{0_u} - \overline{y_0})^2 \tag{32}$$

It is obvious from expression (31) that this sum is associated with the number of degrees of freedom $f_0 = n_0 - 1$. The total residual sum of squares of the plan:

$$s_{\text{заг}} = \sum_{u=1}^{n}(y_u - y_{u_{\text{розр}}})^2 \tag{33}$$

with the number of liberty degrees $f_{заг} = n - \frac{(k+2)(k+1)}{2}$.

The variance of the adequacy of the model is characterized by the sum

$$s_{ад} = s_{заг} - s_0 \tag{34}$$

with the number of liberty degrees

$$f_{a\partial} = n - \frac{(k+2)(k+1)}{2} - (n_0 - 1) \tag{35}$$

Dispersion of adequacy $s^2_{a\partial} = \frac{s_{a\partial}}{f_{a\partial}}$.

The adequacy of the model is checked by Fisher's criterion:

$$F = \frac{s^2_{a\partial}}{s^2_0}. \tag{36}$$

The coefficient will be significant if its absolute value is greater than the possible error. Since it was established using the above formulas that all factors are significant, we can proceed to the analysis of research results and the construction of a nomogram, and obtain an empirical formula.

In order to check the adequacy and compatibility of the calculated mathematical model with the experimental results of thin film synthesis Figure 2 was plotted.

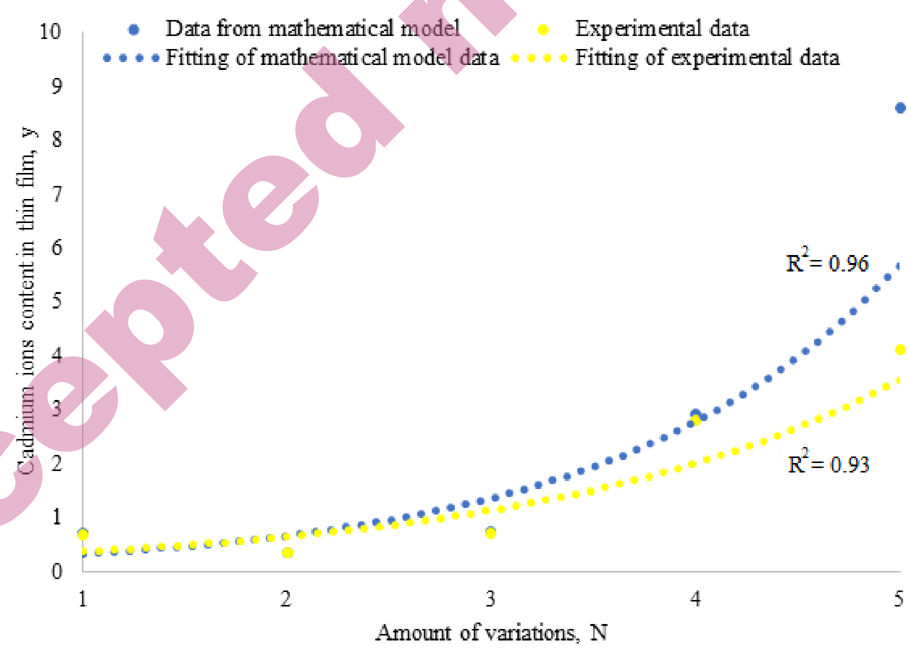

Fig. 2. Comparison of the results of mathematical modeling and experimental synthesis of thin film.

By comparing the R^2 factors of both dependencies, it is evident that the calculated mathematical model is appropriate, as the experimental data align closely with the values predicted by the model.

Based on the analysis of regression coefficients, it can be stated:

- a significant effect on the behavior of the response function is exerted by the factor x_1 (concentration of the initial cadmium containing salt, mol/L), x_3 (process temperature, T, °C), and x_4 (deposition time, t, min), while the factor x_2 (concentration of thiourea, mol/L) does not affect so significantly;

- numerical increase in the concentration of the initial cadmium containing salt; process temperature and the deposition time lead to an increase in the response function and an increase in the concentration of thiourea - to its decrease.

As the regression equation shows, an increase in the 1st, 3rd, and 4th factors leads to an increase in the response function, and an increase in the 2nd factor leads to its decrease.

Based on the results of experimental studies of the content of cadmium ions (Table VI), a nomogram is constructed.[17]

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 selenosulfate concentration – 0.1 mol/L;
– process temperature – 70 °C;
– deposition time – 3 min.[4-5, 7, 18-21]

CONCLUSION

The scientific basics for synthesizing CdS and CdSe semiconductor thin films from aqueous solutions of cadmium-containing salts has been established through mathematical modeling of this process. An important scientific problem of great practical importance has been solved: the optimal conditions for the synthesis of CdS and CdSe thin films by the method of chemical surface deposition using aqueous solutions of cadmium-containing salts: chloride, nitrate, sulfate, acetate, and iodide have been determined. The influence of the nature of the initial salt, process temperature, deposition duration, and the concentrations of salts, thiourea, sodium selenosulfate were studied. A mathematical model of chemical surface deposition of CdS and CdSe thin films as effective photoconverters of solar radiation has been developed. The use of chemically deposited semiconductor materials of the $A^{II}B^{VI}$ type significantly reduces the cost and simplifies the process of creating solar cells, which can become the basis for the mass production of solar cells and solar battery modules. The adequacy of the obtained mathematical model was checked by Fisher's and Cochran's criteria. The optimal synthesis conditions by means of the mathematical calculations were the next: concentration of cadmium-source salt – 0.01 mol/L, chalcogenizer – 1.0 mol/L or 0.1 mol/L in the chase of thiourea or sodium selenosulfate, respectively; temperature – 70 °C and duration of 3 min.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/12637, or from the corresponding author on request.

И З В О Д

МАТЕМАТИЧКИ ПРИСТУП МЕТОДИ СИНТЕЗЕ ПОЛУПРОВОДНИЧКИХ МАТЕРИЈАЛА ФИЛМОВА ТИПА $A^{II}B^{VI}$ ЗА ФОТООСЕТЉИВЕ СТРУКТУРЕ КОЈЕ СЕ КОРИСТЕ ЗА АЛТЕРНАТИВНУ ЕНЕРГИЈУ

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Развијена је научна смерница за синтезу танких филмова CdS и CdSe методом хемијског површинског наношења (CSD), коришћењем раствора са солима које садрже кадмијум: хлорид, нитрат, сулфат, ацетат, и јодид. Да би се поправила ефикасност експеримента и смањили трошкови, развијен је математички модел за CSD процес за CdS и CdSe танке филмове. Модел омогућава одређивање концентрације реагенаса, трајање и температуру CSD, који су потребни за добијање филмова одређене дебљине. Спроведена је оптимизација параметара хемијске депозиције филмастог полупроводничког материјала. На основу математичког модела, оптимални услови за синтезу су следећи: концентрација кадмијумове соли – 0.01 mol/L, халкогенизатор – 1.0 mol/L односно 0.1 mol/L у случају тиоуреe или натријум селеносулфата; температура – 70 °C, и трајање 3 мин. Узимајући у обзир грешке, предложена је математичка зависност резултата експерименталних проучавања од садржаја металних јона у танком филму соларних ћелија за ефикасну директну конверзију сунчевог зрачења у електричну енергију.

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