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Supplementary material

SUPPLEMENTARY MATERIAL TO

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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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:

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

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

The quadratic error is determined:

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

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

$$F = \frac{s_{max}^2}{s_{min}^2}. \tag{S-3}$$

Further, the obtained value of F was compared with the tabular value of Fisher's criterion F_{tabl}. If the tabular value is lower 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 S-I.

Fisher's criterion:

$$F = \frac{0.00000100}{0.00000016} = 6.25. \tag{S-4}$$

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TABLE S-I. Determination of errors in the study of cadmium ions content

№	x_1	x_2	x_3	x_4	y_{cp}	$x_1^2 y_{cp}$	$x_2^2 y_{cp}$	$x_3^2 y_{cp}$	$x_4^2 y_{cp}$	$\Sigma x_i^2 y_{cp}$	$x_1 y_{cp}$	$x_2 y_{cp}$	$x_3 y_{cp}$	$x_4 y_{cp}$	$x_1 x_2 y_{cp}$	$x_1 x_3 y_{cp}$	$x_1 x_4 y_{cp}$	$x_2 x_3 y_{cp}$	$x_2 x_4 y_{cp}$	$x_3 x_4 y_{cp}$	S^2_u x 10^4
1	0.02	0.75	60	2	0.5459	0.55	0.55	0.55	0.55	2.18	-0.55	-0.55	-0.55	-0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.44
2	0.04	0.75	60	2	1.7988	1.80	1.80	1.80	1.80	7.20	1.80	-1.80	-1.80	-1.80	-1.80	-1.80	-1.80	1.80	1.80	1.80	57.46
3	0.02	1.25	60	2	1.3804	1.38	1.38	1.38	1.38	5.52	-1.38	1.38	-1.38	-1.38	-1.38	1.38	1.38	-1.38	-1.38	1.38	0.27
4	0.04	1.25	60	2	1.8434	1.84	1.84	1.84	1.84	7.37	1.84	1.84	-1.84	-1.84	1.84	-1.84	-1.84	-1.84	-1.84	1.84	4.16
5	0.02	0.75	80	2	2.9214	2.92	2.92	2.92	2.92	11.69	-2.92	-2.92	2.92	-2.92	2.92	-2.92	2.92	-2.92	2.92	-2.92	214.92
6	0.04	0.75	80	2	4.57	4.57	4.57	4.57	4.57	18.28	4.57	-4.57	4.57	-4.57	-4.57	4.57	-4.57	-4.57	4.57	-4.57	3.61
7	0.02	1.25	80	2	2.4832	2.48	2.48	2.48	2.48	9.93	-2.48	2.48	2.48	-2.48	-2.48	-2.48	2.48	2.48	-2.48	-2.48	0.18
8	0.04	1.25	80	2	2.8718	2.87	2.87	2.87	2.87	11.49	2.87	2.87	2.87	-2.87	2.87	2.87	-2.87	2.87	-2.87	-2.87	0.55

0.03	135.96	0.02	14.36	14.14	0.77	4.80	2.99	0.67
-1.62	-5.22	-2.52	-4.51	4.31	4.66	2.62	3.83	0.00
-1.62	-5.22	2.52	4.51	-4.31	-4.66	2.62	3.83	0.00
1.62	5.22	-2.52	-4.51	-4.31	-4.66	2.62	3.83	0.00
-1.62	5.22	-2.52	4.51	-4.31	4.66	-2.62	3.83	0.00
1.62	-5.22	2.52	-4.51	-4.31	4.66	-2.62	3.83	0.00
1.62	-5.22	-2.52	4.51	4.31	-4.66	-2.62	3.83	0.00
1.62	5.22	2.52	4.51	4.31	4.66	2.62	3.83	0.00
-1.62	-5.22	-2.52	-4.51	4.31	4.66	2.62	3.83	0.00
-1.62	-5.22	2.52	4.51	-4.31	-4.66	2.62	3.83	0.00
-1.62	5.22	-2.52	4.51	-4.31	4.66	-2.62	3.83	-1.53
6.50	20.88	10.09	18.02	17.25	18.64	10.47	15.32	3.06
1.62	5.22	2.52	4.51	4.31	4.66	2.62	3.83	0.00
1.62	5.22	2.52	4.51	4.31	4.66	2.62	3.83	0.00
1.62	5.22	2.52	4.51	4.31	4.66	2.62	3.83	0.00
1.62	5.22	2.52	4.51	4.31	4.66	2.62	3.83	3.06
1.6242	5.2205	2.5236	4.5054	4.3124	4.6612	2.618	3.829	0.7644
4	4	4	4	4	4	4	4	3
60	60	60	60	80	80	80	80	70
0.75	0.75	1.25	1.25	0.75	0.75	1.25	1.25	1.00
0.02	0.04	0.02	0.04	0.02	0.04	0.02	0.04	0.01
9	10	11	12	13	14	15	16	17

0.90	32.95	3.03	0.01	1.72	3.39	0.81	0.67	2.69
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	-5.83	4.09	0.00	0.00
0.00	0.00	0.00	-2.32	5.66	0.00	0.00	0.00	0.00
0.00	-7.37	4.64	0.00	0.00	0.00	0.00	0.00	0.00
9.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19.42	14.74	9.28	4.64	11.32	11.65	8.18	0.00	0.00
0.00	0.00	0.00	0.00	0.00	11.65	8.18	0.00	0.00
0.00	0.00	0.00	4.64	11.32	0.00	0.00	0.00	0.00
0.00	14.74	9.28	0.00	0.00	0.00	0.00	0.00	0.00
19.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4.8552	3.6845	2.321	1.1608	2.8298	2.9128	2.0438	2.6342	2.6151
3	3	3	3	3	1	5	3	3
70	70	70	50	90	70	70	70	70
1.00	0.50	1.50	1.00	1.00	1.00	1.00	1.00	1.00
0.05	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
18	19	20	21	22	23	24	25	26

0.67	2.76	0.64	18.32	5.57
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00
2.6063	2.6523	2.6155	2.6245	2.6473
3	3	3	3	3
70	70	70	70	70
1.00	1.00	1.00	1.00	1.00
0.03	0.03	0.03	0.03	0.03
27	28	29	30	31

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

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

$$G = \frac{s_{max}^2}{\sum_1^N s_i^2 \frac{0.00000100}{0.00001743}}. \quad \text{(S-5)}$$

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:

$$s^2(y) = \frac{\sum_1^N \sum_1^n (y_i - y_{cp})}{N(n-1)}. \quad \text{(S-6)}$$

Therefore, the reproducibility variance is equal:

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

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 the formula (S-5):

$$s^2(y) = \frac{\sum_1^N \sum_1^n (y_i - y_{cp})^2}{N(n-1)} = \frac{1.27 \cdot 10^{-11}}{31 \cdot (4-1)} = 1.36 \cdot 10^{-13} \quad \text{(S-8)}$$

Regression coefficients were determined by formulas:

$$b_0 = \frac{A}{n}\left[2\lambda^2(k+2)\sum_{u=1}^n y_u - 2\lambda c \sum_{i=1}^k \sum_{u=1}^n x_{iu}^2 y_u\right], \quad \text{(S-9)}$$

$$b_i = \frac{c}{n}\sum_{u=1}^n x_{iu} y_u \quad \text{(S-10)}$$

$$b_{ij} = \frac{c^2}{n\lambda}\sum_{u=1}^n x_{iu} x_{ju} y_u \quad \text{(S-11)}$$

$$b_u = \frac{A}{n}\left\{\begin{matrix} c^2[(k+2)\lambda - k]\sum_{u=1}^n x_{iu}^2 y_u + \\ +c^2(I-\lambda)\sum_{i=1}^k \sum_{u=1}^n x_{iu}^2 y_u - 2\lambda c \sum_{u=1}^n y_u \end{matrix}\right\} \quad \text{(S-12)}$$

In these formulas, the following designations are accepted:

$c = \frac{n}{\sum_{u=1}^n x_{iu}^2}$; $\lambda = \frac{n2^k}{\left(\sum_{u=1}^n x_{iu}\right)^2}$ - for a plan whose core is a full factorial experiment; $\lambda = \frac{n2^{k-1}}{\left(\sum_{u=1}^n x_{iu}\right)^2}$ - for a plan whose core is a semi replicaton of 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 (S-9) - (S-12) calculate all the values that depend on the plan structure, they can be written as:

$$b_0 = \delta_0^{/}\sum_{u=1}^n y_u - \delta_0^{//}\sum_{u=1}^n \sum_{i=1}^k x_{iu}^2 y_u \quad \text{(S-13)}$$

$$b_i = \delta_i \sum_{u=1}^n x_{iu} y_u \quad \text{(S-14)}$$

$$b_{ij} = \delta_{ij}\sum_{u=1}^n x_{iu} x_{ju} y_u \quad \text{(S-15)}$$

$$b_{ll} = \delta_u^{/}\sum_{u=1}^n x_{iu}^2 y_u + \delta_{il}^{//}\sum_{i=1}^k \sum_{u=1}^n x_{iu}^2 y_u - \delta_{ll}^{///}\sum_{u=1}^n y_u \quad \text{(S-16)}$$

The values of δ included in formulas (S-13) - (S-16) can be taken from Table S-I. 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]

The following model is accepted:

$$y_i = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 + x_1^2 + x_2^2 + x_3^2 + x_4^2 \quad \text{(S-17)}$$

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

$$y = (9.00 - 0.91x_4) + (-2.13 + 0.01x_4)p + (0.10 + 0.03x_4)p^2 \quad \text{(S-18)}$$

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 S-II.

TABLE S-II. 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 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:

$$s_{b_0}^2 = \frac{2A\lambda^2(k+2)}{n} s_y^2 \quad \text{(S-19)}$$

$$s_{b_i}^2 = \frac{c}{n} s_y^2 \quad \text{(S-20)}$$

$$s_{b_{il}}^2 = \frac{A[(k+2)\lambda-(k-1)]c^2}{n} s_y^2 \quad \text{(S-21)}$$

$$s_{b_{il}}^2 = \frac{c^2}{n\lambda} s_y^2 \quad \text{(S-22)}$$

Formulas (S-19) - (S-22) 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 S-III.[16]

Experimental error in rotatable planning can be determined by:

$$s_0^2 = \frac{\sum_{u=1}^{n_0}(y_{0u} - \overline{y_0})^2}{n_0 - 1} \quad \text{(S-23)}$$

The numerator of the expression (S-23) is the residual sum of squares in the centre of the plan:

$$s_0 = \sum_{u=1}^{n_0} (y_{0_u} - \overline{y_0})^2 \quad \text{(S-24)}$$

It is obvious from expression (S-23) 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:

$$s_{\text{заг}} = \sum_{u=1}^{n} (y_u - y_{u_{\text{розр}}})^2 \quad \text{(S-25)}$$

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

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

The plan core	γ_0	γ_i	γ_{ii}	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

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

$$s_{ад} = s_{заг} - s_0 \quad \text{(S-26)}$$

with the number of liberty degrees

$$f_{ад} = n - \frac{(k+2)(k+1)}{2} - (n_0 - 1) \quad \text{(S-27)}$$

Dispersion of adequacy $s_{ад}^2 = \frac{s_{ад}}{f_{ад}}$.

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

$$F = \frac{s_{ад}^2}{s_0^2}. \quad \text{(S-28)}$$

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