Mathematical model development for thin zinc oxide film formation with assigned dielectric constant values

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Abstract. This article deals with the problem of the mathematical model development linking the magnetron sputtering technological parameters with the complex dielectric constant of thin zinc oxide films. Computational procedures to calculate the regression equation coefficients are given. The equipment to obtain zinc oxide thin films using the method of reactive magnetron sputtering is described.

1. Introduction
Modern instrument engineering focuses on thin metal oxides films and the technologies to obtain them [1]. Zinc oxide (ZnO) is the best substitute for expensive indium–tin oxide films (In$_2$O$_3$–SnO$_2$). The experiments of many domestic and foreign research teams [1–3] have shown that ZnO possesses better optical properties compared to In$_2$O$_3$–SnO$_2$ and it is a promising optical thin-film material. At present, there are no mathematical models that could be used to predict the optical characteristics of thin zinc oxide films (the refractive index and absorption coefficient to be elements of the complex dielectric constant) depending on the technological methods to obtain them. Thus, the development of the mathematical model linking the technological parameters and the optical properties of thin ZnO films becomes an urgent task.

The aim of the work is to make a mathematical model linking the technological manufacturing parameters with the complex dielectric constant of thin ZnO films.

2. Technological equipment and measuring equipment
Thin ZnO films sputtering of a series of samples was carried out using UVN-71P3 vacuum evaporator adapted for magnetron sputtering. Three major parameters being variable factors were chosen: the gas operating pressure, the oxygen concentration in the working mixture and spray time. The values of other parameters were maintained and measured with the required accuracy: magnetron discharge energy was 0.38 ± 0.02 kW, the distance from the substrate to the target was 100 ± 0.5 mm and the temperature of the substrate was 100 ± 2 °C.

The transmission spectra of thin ZnO films were obtained using SF-2000 spectrophotometer in the wavelength range of 190-1100 nm. The refractive index and absorption coefficient were found with the help of the transmission spectrum using the envelope method to have been described in detail in [4, 5].

We estimated the value of the dielectric constant for each film from the values of the refractive index and transmittance factor. Refractive index $n(\lambda)$ and absorption coefficient $k(\lambda)$ are in the real (1) and imaginary (2) parts of the dielectric constant (3) [6]:

$$
e_1 = n^2 - k^2, \tag{1}$$
\[ e_z = 2nk; \]
\[ e = e_1 - ie_2. \]  

### 3. Mathematical model

The mathematical model of the technological process is the mathematical dependence of the product output indicator \( Y \) on the technological parameters that characterize it \( (X = (X_1, X_2, ..., X_k)) \) [7]. To develop the mathematical model the calculation procedures and their algorithm were taken from [7].

The dependence of the product output indicator \( Y \) on the technological parameters that characterize it \( (X = (X_1, X_2, ..., X_k)) \) is described by the regression equation:

\[
Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i,j=1 \atop i \neq j}^{k} b_{ij} X_i X_j + \sum_{i=1}^{k} b_i X_i^2,
\]

where \( b_0, b_i, b_{ij}, b_{i} \) are the estimated regression equation coefficients; \( k \) is the number of the input parameters. The methods to calculate mathematical models and examples of their application are sufficiently described in [9, 10].

The implementation of the experimental design containing a finite number of experiments allows us to obtain only sample estimates for the coefficients of the equation. Their accuracy and reliability depend on the properties of the sample and they are to be checked.

The values of the variables in the regression equation are represented in the normalized form and have values of +1 and −1. The main task of the experiment planning is the location of the extreme points in the studied area of the factor space in order to obtain the most accurate mathematical description of the object with the minimum number of experiments, which is established by the given optimality criterion of the design.

To make the second-order models that are most suitable for the description of the processes of film coatings formation, papers [8, 9] justify the use of Box–Behnken and Kono Ko23 designs, where the experiments are executed in a specific sequence at points +1, −1.0, −α, α. Here ±α are star points, i.e. the range of factor variation is divided into four sections, respectively, +α refers to the maximum value of the factor, −α is the minimum value of the factor, +1, 0, −1 are points within the variation range. The \( \alpha \) value is calculated using the formula [5]:

\[
\alpha = 2^k, \tag{5}
\]

where \( k \) is the number of input parameters for \( k = 3 \). \( A = 1.682 \).

The calculation of the coefficients of the regression equation and the variance coefficients was performed according to the following formulas [7]:

\[
\begin{align*}
 b_0 &= \frac{A}{N} \left[ \frac{2\lambda_i^2}{N}\sum_{i=1}^{k} Y_i - 2\lambda_i \lambda_j \sum_{i=1}^{k} \sum_{j=1}^{k} X_i X_j Y_i \right]; \\
 b_i &= \frac{\lambda_i}{N} \sum_{i=1}^{k} X_i Y_i (i = 1, k); \\
 b_{ij} &= \frac{\lambda_{ij}}{N^2} \left[ \sum_{i=1}^{k} X_i X_j Y_i (i \neq j = 1, k) \right]; \\
 b_i &= \frac{\lambda_i^2}{N^2} \left[ \sum_{i=1}^{k} X_i^2 Y_i \right]; \\
 b_{ij} &= \frac{\lambda_{ij}^2 (k+2)\lambda_i - k \sum_{i=1}^{k} X_i^2 Y_i + \lambda_i \lambda_j \sum_{i=1}^{k} \sum_{j=1}^{k} X_i X_j Y_i - \lambda_i \lambda_j \sum_{i=1}^{k} \sum_{j=1}^{k} X_i \right]; \\
 b_{ij} &= \frac{\lambda_{ij}^2}{N^2} \left[ \sum_{i=1}^{k} X_i^2 Y_i \right];
\end{align*}
\]

The dielectric constant values, technological parameters of spraying and the corresponding conventional values, according to the experimental design are listed in table 1. The center of the design: pressure (parameter \( X_1 \)) is 1 Pa, oxygen content (parameter \( X_2 \)) is 50 %, sputtering time (parameter \( X_3 \)) is 300 seconds. The response of the model \( Y \) is the dielectric constant \( Y \). The parameters varied within ±0.2 Pa, ±10 %, ±60 s, respectively, the other monitored parameters did not change and they were maintained with a given accuracy.
To check the adequacy, the estimated $F$ values are compared with the table ones. If $F_{estimated} < F_{table}$, the resulting mathematical model can be considered to be adequate with a 95% probability. A test for adequacy has shown that the developed mathematical model for thin zinc oxide films formation with a
given value of the complex dielectric constant can be considered to be adequate with a probability of 0.95 ($F_{estimated} = 2.368 < F_{table} = 2.7$).

The resulting regression equation looks as follows:

$$\varepsilon = 3.923 + 0.52 P_{operating} + 0.03 P_{operating}^2 + 0.251 C_{oxygen}$$

This equation shows that $X_3 = t_s$ parameter (sputtering time), in the range under study, does not affect the dielectric constant of thin zinc oxide films. Other parameters variation of $X_1 = P_{operating}$ (operating pressure) and $X_2 = C_{oxygen}$ (oxygen content in the working mixture) in this range allows one to form thin zinc oxide films having values of complex dielectric constant $\varepsilon$ from 3.2 to 4.8.

4. Conclusions

We have developed the mathematical model of this type: $\varepsilon = 3.923 + 0.52 P_{operating} + 0.03 P_{operating}^2 + 0.251 C_{oxygen}$. It has been proved that $X_3 = t_s$ parameter (sputtering time) in the range under study does not affect the dielectric constant of the obtained thin ZnO films. Varying values of other parameters $X_1 = P_{operating}$ (operating pressure) and $X_2 = C_{oxygen}$ (oxygen content in the working mixture) allows one to form thin ZnO films with dielectric constant values from 3.2 to 4.8.

References

[1] Ghorannevis Z and Hosseinnejad M T 2015 *Theoretical Applied Physics* 8 33–8
[2] Weiqiang S, Yuehui H and Yichuan C 2017 *Advances in Computer Science Research* 76 1790–2
[3] Zaitsev S V and Vashchilin V S 2017 *Bulletin of INRTU* 8 167–75
[4] Brus V V and Kovalyuk Z D 2012 *Technical Physics Journal* 8 110–3
[5] Swanepoel R 1983 *Physics* 16 1215–22
[6] Volpyan O D, Obod Yu A and Yakovlev P P 2010 *Applied Physics* 3 24–30
[7] Guseinov F G and Mamedyarov O S 1988 *Energoatomizdat* 5 139–41
[8] Nalimov V V and Chernova N A 1965 *Science* 7 246–75
[9] Gaskarov D V and Dakhnovich A A 1986 *Higher School* 3 1986–91
[10] Gludkin O P, Obichkin Yu G and Blokhin V G 1977 *Energy* 5 289–96
[11] Barvinyuk V A 1990 *Machine Building* 4 286–384