A Statistical Study About Photocatalytic Properties of Titania Crystals Deposited by Sputtering

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Crystallized titania layers were prepared by vacuum sputtering in a DC magnetron. Photocatalytic properties of the crystals were analyzed using degradation of formaldehyde in a self-conception reactor. All data were analyzed using classical curve dependence and statistical. This study used Anova to find correlations between photocatalytic properties of the crystals and deposition parameters. The considered parameters were pressure, temperature of substrate, argon concentration and time of sputtering, all of this measured during the active process.

Keywords: titania crystals, photocatalysis, statistics, Anova

Photocatalysis is an advanced oxidative process occurring on interface photocatalyst/reaction medium, when photocatalyst is activated by ultraviolet or visible light. It appears because in a semiconductor under irradiation electron-hole pairs are created and subsequent very reactive atomic and molecular species formed on surface are able cu initiate redox reactions [1-3].

Thin layers of titania were fabricated by sputtering using a DC magnetron. Then the photocatalytic activity of the layers was determined in a self-conception reactor, through the ability of degradation of gaseous formaldehyde [4-6].

This study used MLR (multilinear regression) for statistical analysis of data, because the great number of experiments (more than 60) lends an Anova study. Unscrambler X software was the computing instrument. The level *p* of statistical significance and *F* ratio were the parameters used to find correlation between entry-parameters and out-parameters.

Experimental part

Materials and methods

Deposition of titanium dioxide thin layers was performed at room temperature (RT = 20p C), T1 = 100°C, T2 = 200°C and T3 = 300°C, using different rates of admission gas (A3O – argon75%/ oxygen25%; AO – argon50%/ oxygen50% and AA – argon100%), 10, 20 and 30 minutes duration and different pressures (P1=10^4 Pa, P2 = 5‡10^3 Pa, P3 = 10^3 Pa, P4 = 5‡10^2 Pa and P5 = 10^2 Pa). During deposition process direct current was fixed at 300 mA and voltage was around 500 V, which means a deposition power of 150 W. Calculated deposition rates were between 3 and 31.4 nm/min [7].

Degradation of gaseous formaldehyde was described in the doctoral thesis [8]. The evolution of carbon dioxide proving degradation was monitored with a specific sensor. There were performed 60 experimental determinations, because Anova studies require this minimum number.

All experimental data were computed using Origin 8.5 software and the physical dependence of outcome parameters was established using fitting operation applied to experimental curves.

Unscrambler X software was used to perform statistical analysis of experimental data. A value of 2.54 was found using Anova tables for (4; 56) degrees of freedom, because there were 60 experiments and 4 considered parameter.

The *p* level of statistical signification was calculated by software application as an integral of *distribution function F*, for the values superior to *F* (fig. 1). Using a reference value for *p* of 0.05, an inferior value for outcome parameters proves a statistical dependence by entrance parameters, otherwise there were no dependence.

Results and discussions

General reaction for formaldehyde oxidation is:

$$H_2C=O + O_2 \rightarrow CO_2 + H_2O$$

Transformation rate is 1:1, which means that one mol produces one mol of carbon dioxide [9-17].

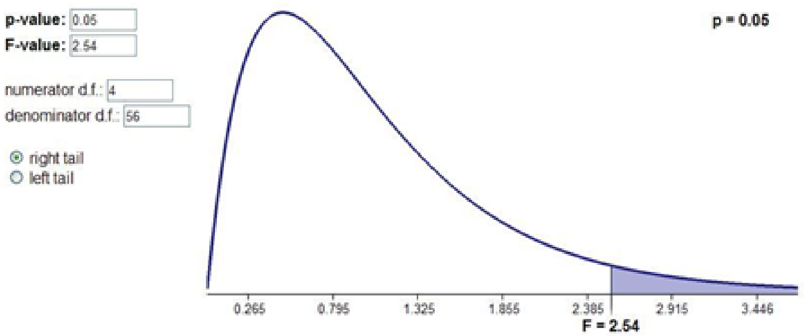

Fig. 1. *F* distribution function for (4; 56) degrees of freedom and 2.54 critical value for parameter of statistical significance *p*

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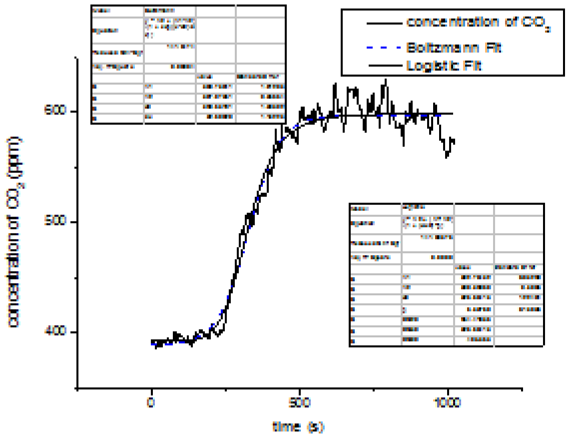

Fig. 2. Example of an imagine of Boltzmann and logistic fit curves obtained on evolution of CO_2 concentration analyzes

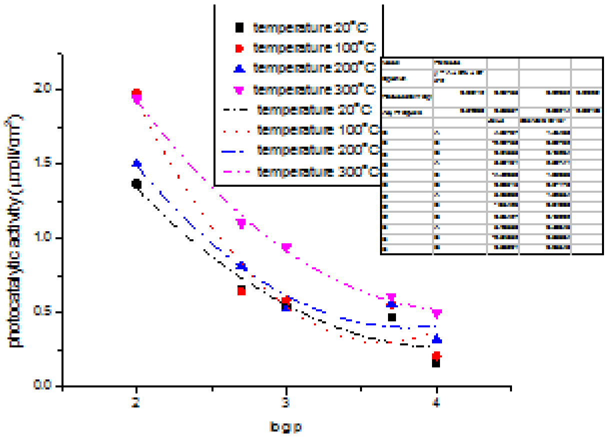

Fig. 3. Photocatalytic activity of layers vs. pressure for different temperatures, for layers deposited in pure argon and 20 minutes. Fitting curves are parabolic

Analyzing CO_2 concentration evolution, logistic curve was those which better described experimental data, being described by equation:

$$y = A_2 + \frac{A_1 - A_2}{\left(1 + \left(\frac{x}{x_0}\right)^p\right)} \qquad (1)$$

where parameters are: A_1, A_2, x_0 and p, and variable x is time. A_1 is minimum concentration of CO_2, A_2 is maximum concentration of CO_2, x_0 is inflection point of logistic curve and p a power exponent. These parameters allowed calculating the photocatalytic activity of layers. The first derivate in x_0 point is:

$$\frac{dy}{dx} = \frac{p(A_2 - A_1)}{4x_0} \qquad (2)$$

This was used to calculate the maximum rate of chemical reaction [9-14].

Analyzes of recorded and calculated data, from represented plots proved that photocatalytic activity depends very strong by pressure of gas during deposition of layers (activity increase when pressure decrease). Also activity depends by temperature and argon concentration, being a positive dependence. A second order polynomial curve (parabola) seems to describe better the dependence of activity by pressure [15-21].

Anova table from figure 4 shows the value 0.000 for the level p of statistical significance for pressure, 0.0005 for temperature and 0.0036 for percent of argon. For instance, these values being inferior to 0.05, one could conclude that these factors have a significant influence on photocatalytic activity of titania layers. The p value for deposition time is 0.0678, gentle superior to 0.05, so deposition time has no influence (or has a very soft one). Regarding F ratio, all those 4 values are superior to critical value (2.54, previously founded). The values for argon percent (9.2234), temperature (13.8550) and pressure (67.0301) are greater than 2.54, therefore (correlated with the values for p), these factors have an evident influence on the photocatalytic activity of the titania layers. The pressure is the most influent parameter.

Similar analyzes found correlation between deposition parameters and calculated maximum reaction rate. There

Table 1

IMAGE OF ANOVA TABLE OBTAINED FOR STATISTICAL ANALYSIS OF DATA REGARDING PHOTOCATALYTIC ACTIVITY OF TITANIA LAYERS FUNCTION BY DEPOSITION PARAMETERS

	Anova Table						
	Multiple Correlation: 0,8051642 (cal) 0,7652251 (val)						
	R-Square: 0,6482894 (cal) 0,5839127 (val)						
	SS	**df**	**MS**	**F ratio**	**p value**	**B-coefficients**	**STDerr**
Summary							
Model	7,7786	4,0000	1,9446	25,8055	0,0000		
Error	4,2200	56,0000	0,0754				
Adjusted Total	11,9986	60,0000	0,2000				
Variables							
Intercept	0,0008	1,0000	0,0008	0,0101	0,9204	-0,0240	0,2392
Ar(%)	0,6951	1,0000	0,6951	9,2234	0,0036	0,0056	0,0018
T (□C)	1,0441	1,0000	1,0441	13,8550	0,0005	0,0013	0,0003
P (barr)	5,0512	1,0000	5,0512	67,0301	0,0000	-7,7693	0,9490
Timp (min)	0,2613	1,0000	0,2613	3,4672	0,0678	0,0171	0,0092

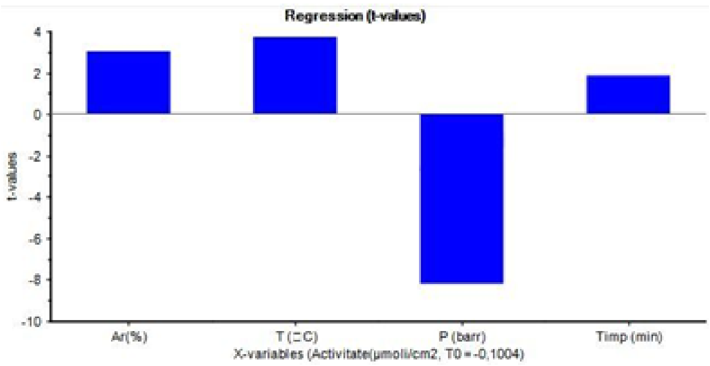

Fig. 4. Regression (t-values in Anova) for photocatalytic activity of titania layers versus deposition parameters

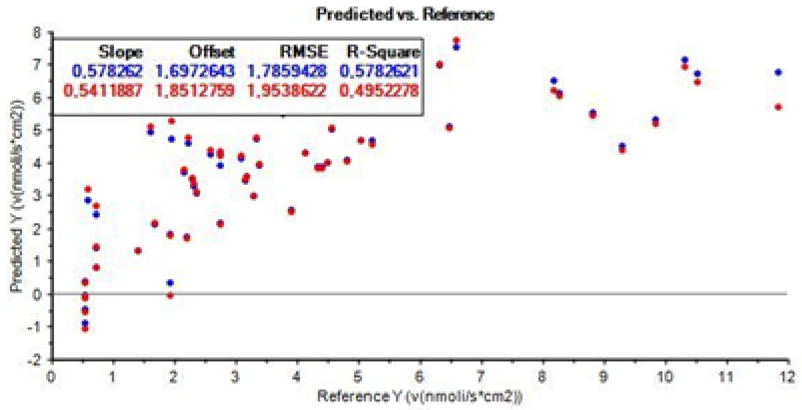

Fig. 5. The predicted values to the reference speed calculated by the reaction of the inflection point of the logistic curve of the titanium dioxide layers on the deposition parameters

were found 0.000 for *p* level of statistical significance for pressure and temperature, 0.1815 for argon percent and 0.5474 for deposition time. So, only pressure and temperature during deposition of titania layers have a significant influence on maximum reaction rate. *F* values for argon percent (1.8302) and deposition period (0.3665) are inferior to critical value of 2.54, then (correlated with *p* values superior to 0.05), these factors do not influence the reaction rate occurring on layers surface. The same strong negative influence of pressure was observed from regression data. Opposite, temperature has a positive influence on photocatalytical reaction rates. Provisioned values are closed to measured ones.

Conclusions

The conclusions of the study are as follow: photocatalytic activity of titania layers depends by pressure, temperature and gas composition during deposition active process; maximum reaction rate on surface of the layers depends by pressure and temperature.

The results of statistical analyzes of data are closed to physical analyzes regarding phenomena (fitting curves).

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