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A STUDY OF THE TEMPERATURE ON THE TiO_2 THIN FILMS SURFACE DEPOSED ON GLASS IN THE MULTIPULSE IRRADIATION REGIME

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Abstract: *This article is based on solving the heat equation in the particular case of thin films of TiO_2 on glass base. The solution of the equation allows establishing the temperature on the film surface within the conditions of multipulse radiation taking into account the glass influence. The rather big values of temperatures are due to incomplete knowledge about the involved values and due to neglecting the consumed energy fractions during the process of vaporization and plasma generation with all the specific effects.*

The outlines graphs on the base of the obtained results present the temperature dependence on the film surface on its thickness, on the number of impulses underlying the influence of the glass on the thermic process that takes place.

Keywords: *titanium dioxide, excimer laser, laser ablation*

1. Introduction

There is currently a large number of works dealing with the scientific and technological properties of TiO_2 [8]. Titanium dioxide is used in applications as diverse as heterogeneous catalysis, photo-catalysis, solar cells, gas sensors, white pigments, corrosion-protective coating, optical coating, ceramics and electric devices. It plays a role in Herat science, biocompatibility. It is discussed as a component in microelectronics and nanotechnology. There is also a need to a better understanding of the physical and chemical properties of the two main crystallographic structures of TiO_2, namely rutile and anatase.

Since TiO_2 is expected to play a role in nano- and microtechnologies, it is interesting to study various methods of nano- and micro-structuring it. Laser treatment is one of the main techniques for designing nano- and microstructures. The irradiation of TiO_2 by laser sources has been report on powders or monocrystals [9-11]. This is shown to induce phase transitions as well as colour changes, due to surface reduction. To our knowledge, laser etching of TiO_2 is not reported in the literature.

Laser interactions with thin films may lead to various processes, like melting, ablation, texturing, hardening [5]. When laser irradiation is performed in air, plasma may be created high fluency, living rise to positive as well as negative feedbacks. Moreover, the processes may be either purely thermic or photolytic. It is then necessary to perform careful experimental studies, in order to a better understanding of the involved physico-chemical mechanisms.

This article is a typical example of using an existent physical model to explain some new experimental observations. It is about the use of the thermic model, based on solving the heat equation, to study the interaction of laser radiation with thin films of TiO_2 on glass base.

2. Experimental details

TiO_2 films are deposited on glass by MSD (Magnetron Sputter Deposition). The coating chamber is an industrial system TSD 400-CD HEF R&D with various facilities such as optical emission and mass spectrometers. The area of the titanium target is $450mm \times 150mm$, its thickness $h = 200\ nm$ and the glass thickness is $8\ mm$. The target is sputtered in dc mode with a ENI RPG 100 generator. The maximum power is $10\ kW$ a maximum voltage of $800\ V$.

The films are irradiated in air, by means of a Lambda Physik (Model Compex 205) excimer laser ($\lambda = 248nm$). The impulse duration is $\tau_P = 25ns$ the impulse energy $E=0{,}13\ J$. The thicknesses of the irradiated films are evaluated by means of a DEKTAK 3030 ST profilometer.

The film has the thickness $h = 200\ nm$ and the area of irradiated surface is constant $S \approx 2\ mm \times 5\ mm = 10^{-5}\ m^2$ (the spot is right-angled).

The experiments consist in the film irradiation in a position with 1 impulse, then in another position with 2 impulses, another one with 3 impulses and so on until 12 impulses.

3. Results and discussions

The irradiated area being identical, the intensities are equals ($I_0 = \frac{E}{S \cdot \tau_P} \approx 5{,}2 \cdot 10^7\ W / cm^2$) and highest enough to produce phase transition of TiO_2 such as sublimation. It is now possible to do an estimation on the involved ablation processes, from the analysis of craters formed by each impulses series. On the other side, for a series of impulses, knowing by profilometric measurements the depth of the crater formed by (j-1) impulses series, it is possible to find the depth of the crater formed by the last impulse of the series with the formula:

$$\Delta h_j = h_j - h_{j+1}\ ,\quad j = \overline{1{,}11} \qquad (1)$$

and the ablation speed by impulse:

$$v_j = \frac{\Delta h_j}{\tau_P}\left(\frac{nm}{puls}\right) \qquad (2)$$

(h_j, h_{j+1} are the film thickness before the j and $j+1$ impulse).

The experimental results, obtained by profilometric measurements, are presented in the next table (table 1):

Table 1. Experimental results obtained by profilometric measurements.

Number of impulses (j)	1	2	3	4	5	6	7	8	9	10	11	12
$h_j(nm)$	200	140	135	77	53	45	37	24	18	25	13	6

Using the values of h_j from table 1 and the relations (1) and (2), result the values of ablation speed corresponding to the irradiation series (table 2):

Table 2. The values of ablation speed corresponding to the irradiation series.

Number of impulses (j)	1	2	3	4	5	6	7	8	9	10	11
$\nu_j(\frac{\text{nm}}{\text{pulse}})$	60	5	58	24	8	8	13	6	-7	12	7

The interpretation of these experimental results is based on a thermic model of interaction between the laser radiation and thin films of TiO_2 on glass base. Therefore, the dependence of space and time of the temperature in target, *T(z,t)*, can be calculated using the heat equation [6], which has the form:

$$\rho c \frac{\partial T}{\partial t} = k_T \frac{\partial^2 T}{\partial z^2} + (1-R)\alpha I_0 e^{-\alpha t}, \qquad (3)$$

where z is the depth in target, t – irradiation time. *P, c, R,* α and I_0, all depending on temperature, representing the density, the specific heat, the reflexivity, the absorption and the intensity of laser radiation on the target surface.

For solving the heat equation have been used, by extrapolation, values for the physical parameters involved at $T = 1500\ K$. The extrapolation was realized, in the case of thermic conductivity (k_T) and thermic diffusivity (χ), by knowing its dependence of temperature till *1200 K* [7,8].

It was neglected the energy fraction required for TiO_2 vaporization and that take over by the plasma generation; the interest was represented by the temperature on the TiO_2 surface in multipulse regime.

The results from extrapolation are: $k_{T_1} = 2{,}66 J/msK$ and $\chi_1 = 0{,}6 \cdot 10^{-6} m^2/s$ for TiO_2, respective $k_{T_2} = 6{,}3 J/msK$ and $\chi_2 = 1{,}75 \cdot 10^{-6} m^2/s$ for glass.

The absorption coefficient was calculated with Fresnel formula:

$$A = 1 - \frac{(n-1)^2 - k^2}{(n-1)^2 + k^2}, \qquad (4)$$

where the refraction index is *n=2,37* [5] and the extinction index *k=1,29* [5]; It results $A = 0{,}73$.

Considering the laser impulse as a superficial heat source (the depth of optical absorption $\delta = \frac{\lambda}{4\pi k}$ = *15 nm* $\langle\langle\ h$), the solution of equation (3) is:

$$T(z,t) = \frac{2AI_0}{K_{T1}}\sqrt{\chi_1 t}\sum_{n=-\infty}^{\infty}\zeta^{|n|}\, ierfc\frac{|z-2nh|}{2\sqrt{\chi_1 t}} \qquad (5)$$

with $I_0 = 5{,}2 \cdot 10^7 W/cm^2$ and $\zeta = \frac{K_{T1}\sqrt{\chi_2} - K_{T2}\sqrt{\chi_1}}{K_{T1}\sqrt{\chi_2} + K_{T2}\sqrt{\chi_1}} = -0{,}16$.

For *z=0* (at surface), $t = \tau_P = 25ns$, *n=2* and because a fraction f=60% from the laser photons energy ($\varepsilon = \frac{hc}{\lambda} \approx 5eV$) is consumed by the transitions of TiO_2 electrons ($E_g = 3\ eV$) [9], the relation (5) become:

$$T_j(z_j = 0, \tau_P) = 13930 \sum\nolimits_j, \quad j = \overline{1,12} \qquad (6)$$

with $\sum_j = \sum_{n=-2}^{2} \zeta^{|n|} ierfc \frac{nh_j}{l_{th_1}}$.

With the formula (6) was determined the temperature at film surface for each impulses series and the results are presented in the table 3.

Table 3. The results of temperature for each impulses

No. of impulses	1	2	3	4	5	6	7	8	9	10	11	12
T_j	7856	7717	7717	7215	6853	6686	6547	6240	6101	6296	5962	5822

The graphs, *T (j), T(h)* and $v(j)$, based on tables 1, 2 and 3, are:

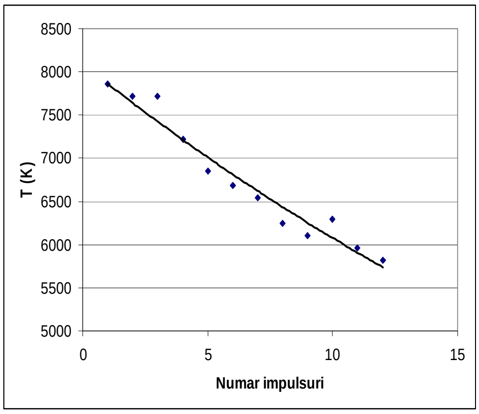

Fig. 1. The dependence of temperature at the film surface of the impulses number

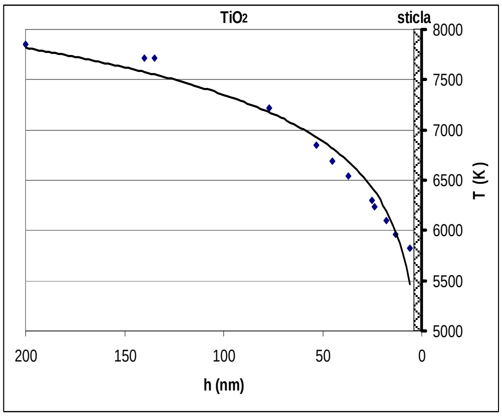

Fig. 2. The dependence of temperature at the film surface of the impulses number

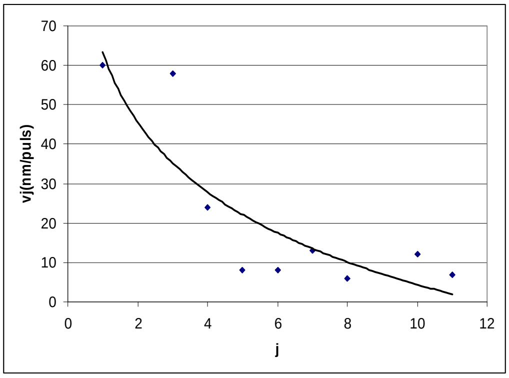

Fig. 3. The dependence of ablation speed of the impulses number

From the graphs analyze results the next conclusions:

1. The dependence *T(h)* shows in which way the glass layer influence the values of the TiO_2 film temperature in it approach. One can observe a higher decrease of this temperature for small film thickness, because of a good thermic conductivity of glass (k_{T2}>k_{T1}) and so because of it's big capacity to take over the heat flux (using a layer with a thermic conductivity smaller then that of TiO_2 will produce a temperature increase at surface while the film thickness decreases).
2. The *t(j)* graph form is the same with that of *v(j)* graph. This fact is normal because the quantity of the irradiated substance depends directly of the temperature on the film surface.

3. The rather big values of obtained temperatures are due to incomplete knowledge about the involved values (thermic conductivity, thermic diffusivity, absorption coefficient) and due to neglecting the consumed energy fractions during the process of vaporization and generating plasma with all the specific effects. It was neglected also the influence of TiO_2 surface roughness on these processes.

The comparison of experimental results from table 2 with theoretical ones can be done with the formula for vaporization speed and also ablation speed at a known temperature [9]:

$$\nu = \nu_0 e^{-\frac{E_{vap}}{KT}} \text{ (atomic layers/ns)} \qquad (7)$$

where: ν - vaporization speed at temperature T, ν_0 - vaporization speed in normal conditions of pressure and temperature (p_0=*1 atm*, *T=273K*), E_{vap} – vaporization energy (on atom or molecule) (in TiO_2 case, E_{vap}*=6,6eV)* [9]) , $K = 1{,}38 \cdot 10^{-23} J/k$ is Boltzmann constant.

To apply formula (7) it is necessary to calculate the value ν_0 for titanium dioxide. So, at a pressure p_0 and a temperature T_{vap}, in the dynamic equilibrium regime set between the number of molecules which leave the free surface in time unit and those which come back on this surface, ν *=1 layer/ns*, neglecting the nature of the substance [10].

Considering, for TiO_2, that $T_{vap} = 3273K$, from equation (7) it is obtained $\nu_0 \cong e^{23}$ *layers/ns* = $25e^{23}$ *layers/pulse* (the pulse duration is τ_P*=25 ns*). Therefore, relation (7) becomes:

$$\nu(T) = 25e^{23-\frac{76520}{T}} \text{ (layers/pulse).} \qquad (8)$$

Analyzing the structure of TiO_2 cell, the thickness of a molecular layer is approximately *0,2 nm* [11]. So:

$$\nu(T) = 5e^{23-\frac{76520}{T}} \text{ (nm/pulse)} \qquad (9)$$

The last expression permits a direct quantitative estimation on the format craters depth if are known the temperatures at surface.

So, if it calculate the first ablation speed for $T_1 = 7856\ K$, it obtain a value to big to be right because of the big value for T_1 (this value is caused by the incomplete knowledge about the used parameters *A*, K_T, χ*)*. It is possible to calculate the necessary value of temperature at surface to produce a crater with the depth Δh_1*=60 nm*, experimental measured, and it obtain $T_1^{'}$*=3734 K =* CT_1, where *C=0,475* and contain information's about the involved parameters (the temperature $T_1^{'}$ was calculated with formula (9), where for ν_1 was used $\Delta h_1 = 60\ nm$).

For the others temperature, it can be used the formula:

$$T_j^{'} = CT_j$$

and to obtain the ablation speeds it is used the formula (9).

The results are presented in table 4 ($\upsilon_{j\,exp}$ are from table 2):

Table 4. The superficial temperatures, the ablation and experimental speeds

Number of impulses (j)	T_j (K)	$\upsilon_{j\ \text{theor.}}\left(\frac{nm}{puls}\right)$	$\upsilon_{j\ \text{exp.}}\left(\frac{nm}{puls}\right)$
1	3734	60	60
2	3665	41	5
3	3665	41	58
4	3427	9,7	24
5	3253	3	9
6	3176	1,7	8
7	3110	1	13
8	2964	0,3	6
9	2898	0,2	-7
10	2990	0,3	12
11	2831	0,1	7
12	2765	0,05	-14

From the graphs, it can be observed a good concordance between theory and experimental results (figure 4):

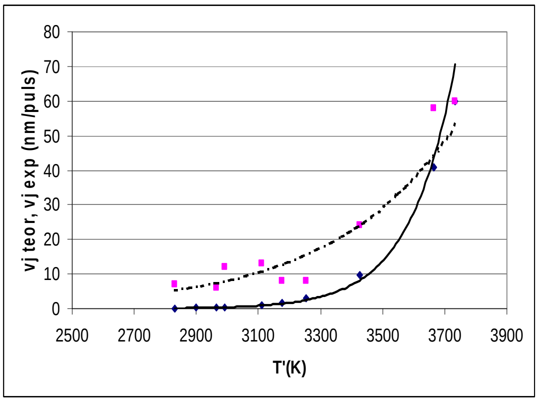

Fig. 4. The dependence of ablation speed of the superficial temperature (pointed line – experimental results; continuous line– theoretical curve)

Another confirmation results from the dependence of ablation speed of impulses number is presented in figure 5:

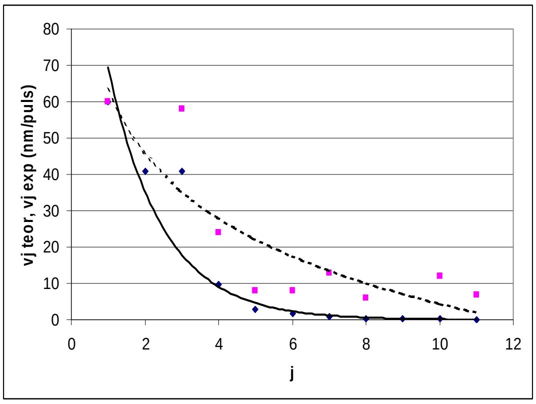

Fig. 5. The dependence of ablation speed of the impulses number

(pointed line – experimental results; continuous line– theoretical curve)

All these results confirm the validity of thermic model which was used and this recommend it in researches for quantitative aspects of ablation process. .

4. Conclusions

The present work shows that, under KrF excimer laser irradiation, sputter deposited TiO_2 films on glass may be ablated. At low fluency, „nothing" occurs (as seen visually and by profilometry). When the fluency increases, one observes a transformation of the system to a thicker film. This is tentatively associated with the crystallization of the initially amorphous film. In the intermediate regime, when the number of pulses increases, one observe progressive ablation of the film. The ablated rate decreases with decreasing film thickness. This is due to a negative feedback effect. At the present time, both thermic and electronic models are quantitatively compatible with the present experimental results. Although the „Occam's razos" principle dictates that the thermic model is the preferred one, more theoretical and experimental work is needed to determine the correct model. Work is in progress in these directions.

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