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Three-dimensional model for oxide thin film growth induced by laser heating of metallic surfaces

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This paper considers the theoretical modeling and the experimental investigation of TiO_2 film growth on Ti films previously deposited over glass substrates. The Ti oxidation occurs due the film surface heating by a moving beam of a pulsed Nd:YAG laser that sweeps the surface at a constant speed of 2 mm/s, under the atmospheric environment. The model takes into account the self-consistent solutions of the three dimensional heat diffusion and oxidation rate equations. Numerical results obtained for 100 and 200 pulses of 290 ns and 3.17 MW/cm^2 with a repetition frequency of 100 and 200 Hz, showed that a maximum temperature of approximately 850 and 1200 K are reached after the action of the fiftieth pulse, respectively. It is observed the occurrence of surface cooling between two consecutive pulses up to the repetition frequency of 100 Hz, and that the surface temperature and the film thickness profiles closely match the gaussian shape of the laser beam space profile. This is a strong indicative that heat diffusion may be neglected during the laser pulse duration. Theoretical predictions for TiO_2 film thickness dependence on laser intensity is in close agreement with the experimental data in the range between 2.4 and 3.2 MW/cm^2.

Keywords: Laser induced oxidation, thin oxide films, laser materials processing.

1. Introduction

Laser induced oxidation process is an important issue in scientific literature since many years ago [1-3] due to its inherent importance for materials processing industry. The main reason is that the laser heating may be extremely localized, opening the possibility for the oxide growth in a pre-determined region with an accuracy of some microns [4], without changing the physical properties of the surrounding environment. Thermochemical modification of Ti films is widely used for optical recording, deposition of masking layers and so on [5]. In the above mentioned applications is very difficult to solve analytically the film's growth equation that can not be decoupled from the heat diffusion equation. Therefore the numerical modeling of the process is much more realistic since one may include many parameters such as the laser scanning speed, the pulse repetition frequency and width, the materials thermal properties, the laser intensity and so on.

This paper considers the theoretical modeling and the experimental study of the oxidation process under the atmospheric environment of the Ti films, previously deposited over glass substrates, due their surface heating by a moving beam of a pulsed Nd:YAG laser. The model takes into account the self-consistent solutions of the three dimensional heat diffusion and the oxidation rate equations under the assumption that the thermal conductivity of the film greatly exceeds the substrate's one. The pulsed laser beam moves at a constant speed being its spot size larger than the film thickness. The temperature and the film thickness profiles are calculated for different laser intensities. The results for film thickness are compared with the experimental data obtained for TiO_2 grown on Ti films in order to probe the accuracy of the adopted model.

2. Theory

In the previous works we presented the analytical approach for the one dimensional model of laser induced oxidation of metallic films [6] and the two dimensional numerical modeling of the same problem faced in a more realistic way, that took into account the translational speed of the laser source as well as the interferometric effects of the laser radiation on the oxide film-metallic substrate interface [7].

In spite of the reasonable agreement between the theoretical predictions and the experimental results some important features of the laser induced oxidation phenomena were not taken into account like the heat loss by black-body radiation. Therefore this paper considers the three dimensional numerical modeling of the laser induced oxidation process considering this important mechanism of sample's heating exchange with the surrounding

environment. In order to deal with this problem we consider the heat flux equation in cartesian coordinates, namely:

$$r_j C_j\left(\frac{\partial T_j}{\partial t} - V_x \frac{\partial T_j}{\partial x}\right) = \nabla(k_j \nabla T_j) + F_j(\mathbf{r},t) \quad (1)$$

here *j=1* refers the metallic surface and *j=2* refers the glass substrate. *r*, *C*, and *k* are the mass density, the specific heat and the thermal conductivity, respectively. *T* is the absolute temperature and V_x is the laser source speed along the x-axis. $F_1(\mathbf{r},t)$ describes the heating source with the loss term and $F_2(\mathbf{r},t)=0$. The heating source is described by:

$$A_1(\mathbf{r},t) = aI(t)A(l)\exp\{\frac{-(x^2+y^2)}{{w_0}^2} - az\} - es\,({T_1}^4(\mathbf{r},t) - {T_E}^4) \quad (2)$$

here *a*, *I(t)*, *A(l)*, w_0, *e*, and *s* are the absorption coefficient, the laser intensity, the absorvity of the layered metal-oxide film of thickness *l*, the laser spot size, the material emissivity and the Stefan-Boltzmann constant respectively. $T_1(\mathbf{r},t)$ and T_E are the temperature of the metallic surface and the surrounding environment respectively.

Equation (1) does not describe the oxidation phenomenon. Therefore the model adopted considers the parabolic law of oxidation, i.e. [3]:

$$\frac{dl}{dt} = \frac{d_0}{l}\exp\{-T_D / T_1(x,y,z,t)\} \quad (3)$$

here d_0 is the ionic diffusion coefficient in the oxide film, *l* is the oxide layer thickness and T_D is the ionic diffusion activation temperature in the oxide in Kelvin degrees . The self consistent solutions of equations (1) and (3) give the complete description of the oxide growth under the laser action. The beam intensity is given by:

$$I(t) = I_0 t_0 \sum_{m=0}^{\infty} d(t - mt) \quad (4)$$

Here I_0, t_0 and *t* are the peak intensity, the pulse width, the inverse of the repetition frequency, respectively. The δ function may be represented by:

$$d(t-m\,t) = \begin{cases} 0 & t-m\,t < -1/2\,h \\ h & -1/2\,h < t-m\,t < 1/2\,h \\ 0 & t-m\,t > 1/2\,h \end{cases} \quad (5)$$

where $h = 1/t_0$.

The absorptivity of the layered metal-oxide film of thickness *l*, *A(l)* is given by:

$$A(l) = 1 - |R(l)|^2 \quad (6)$$

where *R(l)* is the reflectivity of the layered metal oxide film. For the case of normal incidence we have [7]:

$$R(l) = \frac{r_{12}e^{-2iy} + r_{23}}{e^{-2iy} + r_{12}r_{23}} \quad (7)$$

being

$$r_{12} = \frac{1-\sqrt{e}}{1+\sqrt{e}} \quad (8)$$

$$r_{23} = \frac{r_{12} - r_{13}}{r_{12}r_{13} - 1} \quad (9)$$

$$r_{13} = \sqrt{1 - A_0} \quad (10)$$

and

$$y = \frac{2pnl\sqrt{e}}{c} \quad (11)$$

where *i= Ö-1*, *n = c/l*, being *c* and *l* the speed of light and the laser radiation wavelength respectively. r_{12} and r_{13} are the amplitude reflection coefficients from the oxide and from the metal respectively, A_0 is the absorptivity of the metal without the oxide film. The dielectric constant is given by *Öe=n+ik* where *n* and *k* are the refraction index and the extinction coefficient for the oxide.

The numerical solution of equation (1) took into account the following boundary conditions:

$$T_1(x,y,z,0) = T_2(x,y,z,0) = T_E \quad (12)$$

where T_E is the environment temperature

$$\frac{\partial T_j(0,y,z,t)}{\partial x} = \frac{\partial T_j(x_0,y,z,t)}{\partial x} = 0 \quad (13)$$

$$\frac{\partial T_j(x,0,z,t)}{\partial y} = \frac{\partial T_j(x,y_0,z,t)}{\partial y} = 0 \quad (14)$$

being x_0 and y_0 the substratum length and width respectively. Here *j=1* corresponds to the metal and *j=2* to the glass substrate. The boundary conditions at the film-substrate interface are:

$$k_1 \frac{\partial T_1(x,y,z_1,t)}{\partial z} = k_2 \frac{\partial T_2(x,y,z_1,t)}{\partial z} = 0 \quad (15)$$

and

$$T_1(x,y,z_1,t) = T_2(x,y,z_1,t) \quad (16)$$

being z_1 the thickness of the metallic film. The heat flux at the substratum base ($z=z_a$) is equal to zero, i.e.:

$$k_2 \frac{\partial T_2(x,y,z_a,t)}{\partial z} = 0 \quad (17)$$

3. Experimental

The growth of the TiO_2 films was performed on Ti thin films (thickness of ≈ 1000 Å) deposited over microscope glass slices through the evaporation method. The oxidation of Ti was performed using a Nd:YAG Laser (Spectra Physics 3800 S) operating in the Q-switching-Mode-Locked regime. In this regime the laser output is composed by a pulse train with an overall envelope of 290 ns and with individual pulses typically of 100 ps. The peak intensity varied from 2 to 4 MW/cm^2. The sample movement was realized by a computer controlled x-y translator. The oxidation processes driven by the laser surface heating under the atmospheric environment produced TiO_2 tracks over the Ti films due its translation at a constant speed of 2 mm/s. The TiO_2 track surface's profiles were determined using a microprofiler Tencor Alpha-Step 100^{TM} with an accuracy of 10 Å. The results obtained for film thickness was further compared with the theoretical values for the same set of experimental parameters. The chemical composition of the tracks was determined from micro-Raman spectra of the samples obtained using the 514.5 nm line of an Ar ion laser (Coherent 90-5), operating in the power range from 300 to 400 mW. Most of the spectra were recorded using a 600 groves/mm diffraction grating that gave a spectral resolution of 3 cm^{-1}. The results confirmed the formation of TiO_2 showing that the experimental conditions favoured this oxide stoichiometry.

4. Results and Discussions

Fig. 1 shows the time dependence of the surface temperature. It is observed that the temperature reaches the maximum value of 1240 K after 0.5 s of exposure time to the laser beam for a pulse repetition frequency of 200 Hz and the incidence of 200 pulses. The scanning laser speed was kept constant in 2 mm/s. For this frequency is observed that the maximum temperature reaches a stationary regime during the laser action. This is an strong indicative that for such pulse repetition frequency the loss mechanisms are not enough to cool down the surface temperature during the time interval between two consecutive pulses. The maximum temperature reached

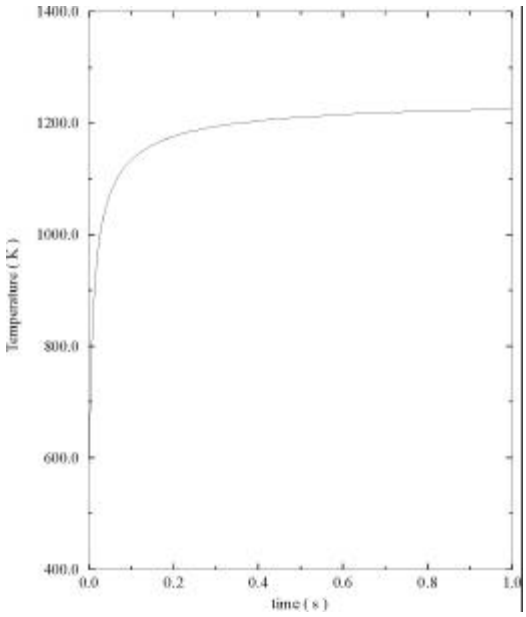

Fig.1.Time dependence of the surface temperature for the pulsed laser beam. The pulse repetition frequency is 200 Hz, the number of pulses is 200 and the pulse duration is 290ns.The laser scanning speed was kept fixed in 2 mm/s.

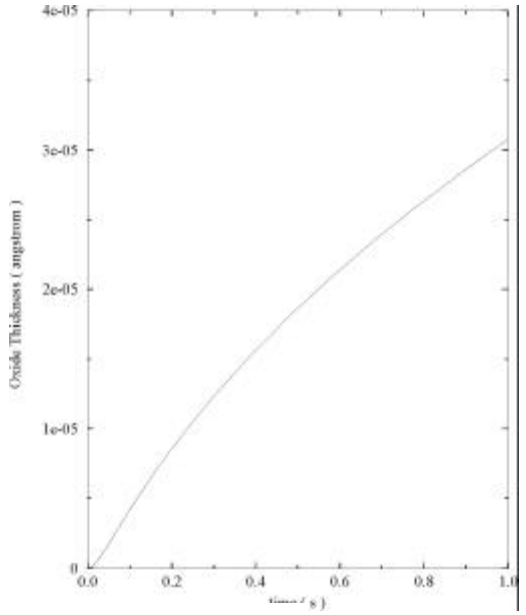

Fig. 2. Time dependence of oxide thickness for the pulses characteristics presented in figure 1.

under such condition is compatible with the threshold temperature for TiO_2 formation. Fig. 2 shows the time dependence of the oxide thickness for the laser pulse characteristics presented in Fig. 1. It may be observed that the oxide thickness reaches a value of 0.3 μm after 1 s of exposure to the laser action. This result is in good agreement with the film thickness measured with the micro profiler.

Fig. 3 shows the TiO_2 track profile for the same experimental condition showed in Fig. 1. It may be observed that the oxide track profile closely matches the laser beam space profile indicating that the heat diffusion out the region exposed to the laser beam is negligible in a time scale comparable with the laser pulse duration. In fact, the thermal diffusion length is approximately 2,32 μm for τ_0 = 290 ns.

The results obtained for the TiO_2 thickness dependence on laser intensity is shown in Fig. 4. It can be seen that the oxide thickness increases monotonically as the laser peak intensity varies from 2.4 to 3.17 MW/cm^2. The theoretical curve resulted from the integration of equation (3), is in close agreement with the experimental data. These results

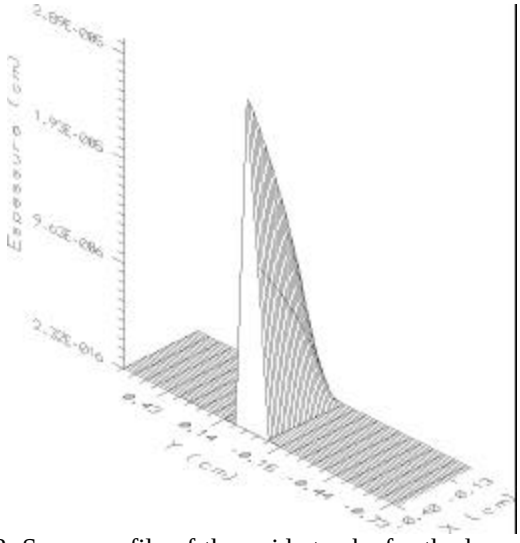

Fig. 3. Space profile of the oxide tracks for the laser beam characteristics presented in figure 1. It may be seen that the track profile closely matches the laser beam space profile.

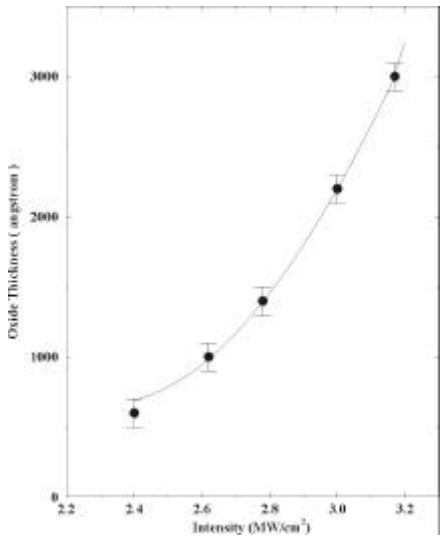

Fig. 4. Oxide Thickness dependence on laser intensity for 200 laser pulses, (τ = 290ns, f=200Hz, v_x = 2 mm/s). The full line corresponds to theoretical values, and the dots to the experimental data.

show that the parabolic law for the film growth is effective in the description of the oxidation processes of Ti films due to heating caused by a moving pulsed laser beam, taking into account the heating loss by black-body emission.

Conclusions

This paper showed the effectiveness of the phenomenological description of the oxidation process of Ti films due the surface heating by a moving pulsed laser beam. The numerical approach adopted for the self-consistent solution of the heat diffusion equation coupled with the parabollic growth law was effective in the prediction of the TiO_2 film thickness for the parameters used in the experiments. These results showed that is possible to predict the thickness of an oxide film with a reasonable accuracy using the present model. It also should be pointed out that such control of the experimental parameters is necessary for the use of this technique in microlitography process where high accuracy patterning capability is of key importance.

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