Diffraction-aided laser-induced microstructuring of thin TiO$_2$ films on glass

O. Van Overschelde and M. Wautelet[a]
Condensed Matter Physics, University of Mons-Hainaut, 23 Avenue Maistriau, B-7000 Mons, Belgium

Thin films of TiO$_2$ are deposited by magnetron sputtering on glass substrate and are irradiated by ultraviolet radiation using a KrF excimer laser. These thin films are patterned with a razor blade placed in the way of the radiation. When the fluence is in the 1250–1550 mJ/cm^2 range, a regular structure appears, with controlled ablation of the films. It is shown that above a critical local fluence, the ablated depth varies linearly with the local fluence. The proportionality factor is shown to be equal to two photons per evaporated molecule. © 2006 American Institute of Physics.
[DOI: 10.1063/1.2364462]

There is currently a large number of works dealing with the scientific and technological properties of TiO$_2$.[1,2] Titanium dioxide is used in applications as diverse as heterogeneous catalysis, photocatalysis, solar cells, gas sensors, white pigments, corrosion-protective coating, optical coating, ceramics, and electric devices. It plays a role in earth science and biocompatibility. Since TiO$_2$ is expected to play a role in nano- and microtechnologies, it is interesting to study various methods of nano- or microstructuring TiO$_2$. Laser treatment is one of the main techniques for designing nano- and microstructures. The irradiation of TiO$_2$ by laser sources has been reported on powders, monocrystals,[3–5] and thin films.[6] This is shown to induce phase transitions (crystallization and ablation) as well as color changes due to surface reduction.

The physicochemical mechanisms of laser-induced transformations of TiO$_2$ are not yet fully understood. Laser interactions with thin films may lead to various processes, such as crystallization, melting, ablation, texturing, and hardening.[7] When laser irradiation is performed in air, plasmas may be created at high fluence F, giving rise to positive as well as negative feedbacks. Moreover, the processes may be either purely thermal or photolytic. It is then necessary to perform careful experimental studies in order to better understand the involved physicochemical mechanisms.

One way is to perform systematic studies of laser treatment as a function of F. It has been shown that it is possible to pattern nanostructured films by irradiating Ag films by a diffraction controlled nonuniform laser beam.[8] This leads to performing morphological changes at the percolation transition. In this letter, we show that it is possible to control the ablation of thin TiO$_2$ films on glass by diffraction-aided laser-induced processing. Moreover, this allows us to obtain different irradiation conditions under one experiment. In turn, this gives information on the physicochemical mechanisms involved in laser ablation of thin films.

TiO$_2$ films are deposited on glass by magnetron sputter deposition. The coating chamber is an industrial system (TSD 400-CD HEF R&D) with various diagnostic facilities such as optical emission and mass spectrometers. The area of the titanium target is 450×150 mm^2. The target is sputtered in continuous mode with an ENI RPG 100 generator. The maximum power is 10 kW with a maximum voltage of 800 V. In the following, the experiments are performed on 208 nm thick TiO$_2$ films on glass (area: 7.5×24 cm^2).

The films are irradiated in air by means of a Lambda Physik (Model Compex 205) excimer laser emitting at a wavelength $\lambda = 248$ nm. The pulse duration is given to be $\tau = 25$ ns. The laser fluence is changed by varying the distance between an ultraviolet lens (focal length=250 mm) and the sample.

In order to produce nonuniform and well characterized spatially resolved laser irradiation, a razor blade is placed in contact with the films. The distance between the edge of the razor blade and the film is measured to be equal to 55 μm. This experimental setup gives rise to a border diffraction effect, hence a nonuniform but well known irradiation pattern. F is varied between 100 and 1550 mJ/cm^2. After irradiation, the thicknesses of the irradiated films are evaluated by means of a Dektak 3030ST profilometer.

Typical optical microscope images and the corresponding profilometry measurements of the irradiated films are given in Figs. 1 and 2, respectively. Four main regimes are observed. In the following, we report on single-shot irradiations. At low F (<100 mJ/cm^2), no transformation takes place, as seen visually and measured by profilometry. Increasing F, at $F \sim 100$ mJ/cm^2, some transformation occurs, as seen visually. The structure follows the local laser fluence. Profilometry measurements indicate that the total thickness of the films increases by 10–100 nm above the starting level. At these low fluences, the laser-irradiated films are thicker than the original films. A similar behavior is observed in the same fluence range in the case of uniform excimer-laser irradiation.[6] This is tentatively associated with the crystallization of the initially amorphous film. Although the lateral characteristics of the structure mimic the diffraction pattern,
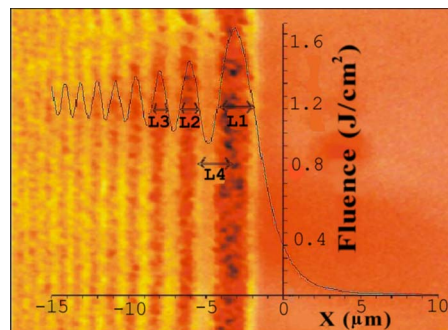

FIG. 1. Optical microscopy of the diffraction-aided ablated structure.

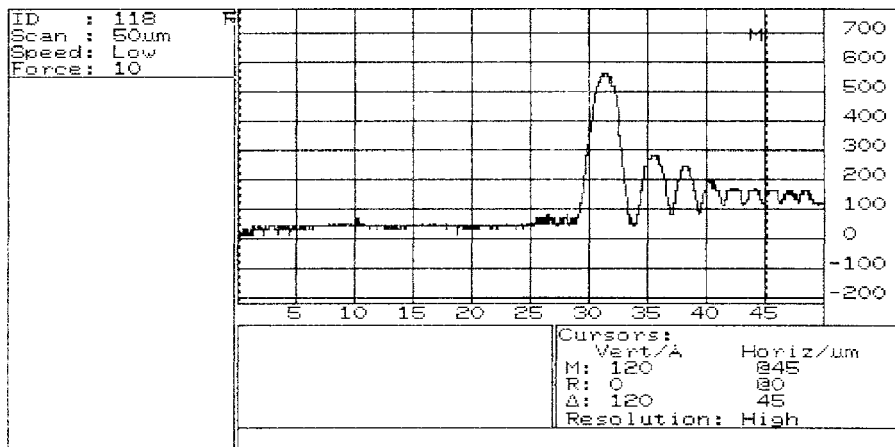[a]Electronic mail: michel.wautelet@umh.ac.be

FIG. 2. Profilometry measurement ($F = 1250$ mJ/cm^2).

hence allowing controlled spatial structuring of the irradiated films, it is not yet possible to relate the thickness variations with the fluence oscillations.

When F increases further, a complex structure is observed. When F attains a value of 1250 mJ/cm^2, the regular structure appears, with controlled ablation of the films. At very high F (>1550 mJ/cm^2), films detach from the substrate.

Let us now examine results obtained in the ablation regime (1250 mJ/cm$^2 < F < 1550$ mJ/cm^2). Let x be the spatial coordinate in the direction perpendicular to the razor border edge. In the first step, the $F(x)$ variation is calculated at the film level by the diffraction theory,[9]

$$F = \frac{F_0}{2}\left\{\left[\frac{1}{2} - C(\nu)\right]^2 + \left[\frac{1}{2} - S(\nu)\right]^2\right\}. \qquad (1)$$

In this equation, F_0 is the incident fluence of the laser beam, and $C(\nu)$ and $S(\nu)$ are the real and imaginary parts of the complex Fresnel integral, respectively; ν is the Fresnel parameter

$$\nu = x\sqrt{\left(\frac{2}{D\lambda}\right)}, \qquad (2)$$

where λ is the laser wavelength and D is the razor edge–film distance. A typical $F(x)$ curve is shown in Fig. 1.

In the second step, the positions of the maxima and minima of $F(x)$ are compared with the minima and maxima of the profilometer results, as shown in Fig. 1, for $F_0 = 1250$ mJ/cm^2 and $D = 55$ μm. The distances L1–L4 (see Fig. 1) are calculated to be equal to 2.16, 1.23, 0.82, and 1.69 μm, respectively. The corresponding measured distances are equal to 2.5, 1.29, 1.00, and 2.21 μm (± 0.2 μm), respectively. This implies that it is possible to structure the film thickness profile laterally in a controlled manner.

In the third step, $F(x)$ is compared with the local ablated depth $Z(x)$ of the films. In the evaluation of $Z(x)$, it is assumed that $Z = 0$ at the maximum height of the film (see Fig. 2). It is expected that, prior to ablation, the film thickens in the irradiated zone, such as observed at $F < 1250$ mJ/cm^2. The variation of Z with F (taken at various x) is shown in Fig. 3. It turns out that Z varies linearly with F,

$$Z = A(F - F_1). \qquad (3)$$

It turns out that $A^{-1} = 0.57 \times 10^{11}$ J m^{-3} and $F_1 = 1.0$ J cm^{-2}. This implies that in this regime, it is possible to control locally the film thickness.

Let us now look at the physicochemical mechanisms. In a previous work,[6] it has been argued that the excimer-laser ablation of TiO$_2$ films may be explained either by a thermal model or by electronic effects or by a combination of both. The starting point of any laser-induced effect is the absorption of electromagnetic energy by the solid. Part of the electromagnetic energy is reflected by the surface. The initial reflectivity R is easily calculated via the knowledge of the complex refractive index of the film at the irradiating wavelength.[10] In our case, $R = 0.27$ near room temperature. The nonreflected energy is absorbed within a thin layer characterized by the optical absorption depth δ obtained from the optical constants of the film. Here, $\delta = 15$ nm. Since the thickness of the film is higher (208 nm) than δ, the energy is entirely absorbed in the film.

The absorption of light occurs by excitation of electrons from occupied to unoccupied energy states. When the photon energy $h\nu$ is larger than the fundamental band gap E_g the main absorption paths couple delocalized states. In our case, $h\nu = 5$ eV $> E_g \approx 3$ eV. The optically excited states are obviously unstable. The system decays by a combination (spatial and temporal) of various processes involving electrons, phonons, and atoms (or vacancies). This results in heating of the lattice. When heating is sufficient, phase transitions (melting and vaporization) may occur. When both δ and the heat diffusion length L_T are much lower than the dimensions of the irradiated sample, laser heating may be viewed as localized at the irradiated surface. In our case, $L_T = (D_{th}\tau)^{1/2}$, where D_{th} is the thermal diffusivity. At room temperature, $L_T = 180$ nm. Since D_{th} is known to decrease with increasing temperature, L_T is less than this value under laser irradiation conditions. In the case of a film-substrate system, when the
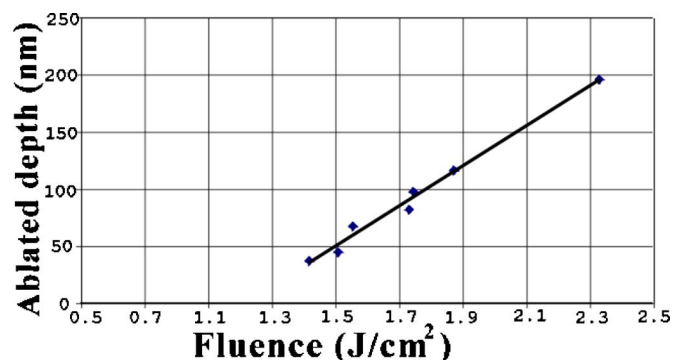

FIG. 3. Variation of the ablated depth with the local fluence.

thickness of the film cannot be neglected (i.e., the heat diffusion through the interface cannot be neglected), the temperature T is given by[7]

$$T(z,t) = [(1-R)I/k_1]\left[(4\chi_1 t)^{1/2}\sum_n \xi^{|n|} i\, \mathrm{erfc}[|z \right.$$
$$\left. - 2nh|/(4\chi_1 t)^{1/2}]\right], \tag{4a}$$

$$\xi = [k_1(\chi_2)^{1/2} - k_2(\chi_1)^{1/2}]/[k_1(\chi_2)^{1/2} + k_2(\chi_1)^{1/2}]. \tag{4b}$$

In these equations, t is the time and I is the effective fluence by unit time (expressed in W cm^{-2}). In the case of a semiconductor, $I = F(h\nu - E_g)/h\nu$. The factors k_1 and k_2 are the thermal conductivities of the film and the substrate, respectively; χ_1 and χ_2 are the heat diffusivities of the film and the substrate, respectively. z is the distance from the film-air interface.

In order to evaluate T by means of Eqs. (4), it is necessary to know the values of the optical and thermal properties of the film and the substrate at high temperature. Unfortunately, these are not known at the highest temperatures calculated in the present work. In order to obtain orders of magnitude T, the high temperature thermal parameters are extrapolated by a power function fit (ORIGIN 7.0 software) from the data given in the literature (up to 1500 K).[2,10] Taking into account the latent heats for melting and evaporation, the maximum value of $T(0,t)$ is calculated to be equal to about 5500 K at F_1. Given the uncertainties in the thermodynamic parameters of the film and the substrate at high temperature, we tentatively associate F_1 with the evaporation temperature [above 3200 K (Ref. 11)] of TiO$_2$. In other words, F_1 would correspond with the evaporation of the surface of the film.

When $F > F_1$, another mechanism takes place. It is worth noting that the constant A^{-1} in Eq. (3) corresponds exactly to two photons per evaporated molecule. This implies that two photons are necessary to break the chemical bonds. This proportionality is similar to what is observed in excimer-laser-induced photoablation of polymers or biological materials.[12]

There are different mechanisms relevant to surface effects. One of them is the breaking of surface chemical bonds responsible for evaporation. In the framework of the modeling of photoassisted surface effects, it has been argued[13] that the cohesive properties of electronically excited states are different from the ones of nonexcited ones. The overall desorption rate depends on the number of electronically excited states. This is expected to be proportional to the instantaneous number of photoexcited electrons, f. Altogether, the total evaporation rate R_{tot} is the sum of the nonexcited R_{ne} and excited R_e contributions,

$$R_{tot} = R_{ne} + R_e = R' + fR''. \tag{5}$$

Let us assume that the photoexcited sites are characterized by a higher ablation rate than the nonexcited ones, i.e., $R'' > R'$. In this case, the higher the number of excited electrons, the higher the ablation rate. Moreover, the ablation rate varies linearly with F since F is proportional to f. This explains qualitatively the variation of the ablated depth Z with F. Further theoretical and experimental works are needed in order to obtain a complete understanding of the origin of this effect.

Whatever the theoretical interpretation, the present work shows that it is possible to control locally the structuring of thin TiO$_2$ films on glass by diffraction-aided excimer-laser irradiation. Moreover, using this method, one may obtain various irradiation conditions in one experiment, due to the nonuniform laser irradiation.

[1]Y. Leprince-Wang and K. Yu-Zhang, Surf. Coat. Technol. **140**, 155 (2001).
[2]U. Diebold, Surf. Sci. Rep. **48**, 53 (2003).
[3]T. Le Mercier, J.-M. Mariot, P. Parent, M.-F. Fontaine, C. F. Hague, and M. Quarton, Appl. Surf. Sci. **86**, 382 (1995).
[4]T. D. Robert, L. D. Laude, V. M. Geskin, R. Lazzaroni, and R. Gouttebaron, Thin Solid Films **440**, 268 (2003).
[5]Y.-J. Li, T. Matsumoto, N. Gu, and M. Komiyama, Appl. Surf. Sci. **237**, 374 (2004).
[6]O. Van Overschelde, S. Dinu, G. Guisbiers, F. Monteverde, C. Nouvellon, and M. Wautelet, Appl. Surf. Sci. **252**, 4722 (2006).
[7]D. Bauerle, *Laser Processing and Chemistry* (Springer, Berlin, 2000), 155.
[8]E. Haro-Poniatowski, E. Fort, J. P. Lacharme, and C. Ricolleau, Appl. Phys. Lett. **87**, 143103 (2005).
[9]F. Graham Smith and T. A. King, *Optics and Photonics: An Introduction* (Wiley, Chichester, 1999), 153.
[10]*Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, Orlando, 1985), 795.
[11]*CRC Handbook of Chemistry and Physics*, 67th ed., edited by R. C. Weast (CRS, Boca Raton, FL, 1986), B-140.
[12]I. W. Boyd and R. B. Jackman, *Photochemical Processing of Electronic Materials* (Academic, London, 1992).
[13]M. Wautelet and E. D. Gehain, Semicond. Sci. Technol. **5**, 246 (1990).