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Excimer laser ablation of thin titanium oxide films on glass

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Abstract

Thin titanium dioxide films are deposited on glass substrates by magnetron sputter deposition. They are irradiated in air, by means of a KrF excimer laser. The ablation rate is measured as a function of the laser fluence per pulse, F, and of the number of pulses, N. Above a fluence threshold, the films are partially ablated. The ablated thickness does not vary linearly with N. This is the signature of a negative feedback between the film thickness and the ablation rate. The origin of this negative feedback is shown to be due to either thermal or electronic effects, or both. At high F, the film detachs from the substrate.

Keywords: Titanium dioxide films; Glass substrates; Magnetron sputter deposition; Laser processing; Thin films; Laser ablation

1. Introduction

There is currently a large number of works dealing with the scientific and technological properties of TiO_2 [1]. Titanium dioxide is used in applications as diverse as heterogeneous catalysis, photocatalysis, solar cells, gas sensors, white pigments, corrosion-protective coating, optical coating, ceramics, electric devices. It plays a role in earth science, biocompatibility. It is discussed as a component in microelectronics and in nanotechnology. There is also a need to better understand 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- or microstructuring it. 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 or monocrystals [2–4]. 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, plasmas may be created at high fluence, 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 physico-chemical mechanisms.

It is the aim of this work to study experimentally, the mechanisms associated with the excimer laser treatment of TiO_2 films deposited on glass.

2. Experimental details

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 area is 450 mm × 150 mm and its thickness 8 mm. The target is sputtered in dc mode with a ENI RPG 100 generator. The maximum power is 10 kW with a maximum voltage of 800 V. In the following, the experiments are

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performed on 208 nm thick TiO_2 films on glass (area: 7.5 cm × 24 cm).

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

The thicknesses of the irradiated films are evaluated by means of a DEKTAK 3030ST profilometer.

3. Experimental results

3.1. Irradiation by one pulse of varying laser fluence

The TiO_2/glass systems are first irradiated by one pulse of varying fluence, F. At low F, no transformation takes place, as seen visually and measured by profilometry. Increasing F, at $F = 0.86$ J/cm^2, some transformation occurs, as seen visually. The film transforms from transparent to translucide. When F attains a value of 1.44 J/cm^2, films detach from the substrate. The detached films appear as free flat ones. This indicates that the detached films are not molten. These films are analysed by electron microscopy and diffraction. Characteristic electron microscopy images and diffraction rings are shown in Fig. 1. The films are made of rutile-type crystals, in the 50–150 nm range.

3.2. Irradiation by many pulses at a fixed laser fluence

Films on glass are then irradiated at a fixed laser fluence, by a varying number of pulses. We report here on $F = 1.3$ J/cm^2, i.e. below the sudden detachment threshold. The variations of the thickness and the surface roughness with the number of pulses, N, are shown in Fig. 2. After one pulse, the thickness and the roughness of the surface increase drastically. Starting from $N = 2$, the film is progressively ablated. However, the ablated thickness per pulse (or ablation rate) decreases with increasing N. This implies that there is a negative feedback between the remaining thickness of the film and the ablation rate. Moreover, the fact that the roughness also decreases with increasing N shows that it has also to be included in any modeling of the ablation process.

It is worth noting that this negative feedback is opposite to most experimental results reported in the literature on excimer laser irradiation of thin films on substrates, where positive feedbacks are the rule [5].

4. Discussion

The previous results indicate that there is a negative feedback between the film thickness and the ablation rate, at fixed laser fluence. Such negative feedbacks have also been observed elsewhere. The main physical reasons proposed in the literature are related to (a) the optical absorption depth, (b) the formation of a plasma in the irradiated atmosphere, (c) the roughness of the transforming surface, (d) heat diffusion and (e) electronic effects. Let us now look at these various effects in the framework of our experimental results. Here, we discuss the negative feedbacks observed during the ablation up to $N = 5$–6.

4.1. Negative feedback

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 [6]. In our case, $R = 0.27$. The non-reflected 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. When the thickness of the irradiated film, h, compares to or is smaller than δ, part of the energy arrives at the film–substrate interface, and less energy is absorbed in the film, giving rise to a decrease of the induced temperature, T. Since the decrease of the ablation rate is higher at high h, this rules out the mechanism (a), above.

When the film transforms, one observes a variation of the surface roughness. It is expected that when this roughness increases the reflected part of the beam increases; hence, the absorption decreases, giving rise to a negative feedback. In our

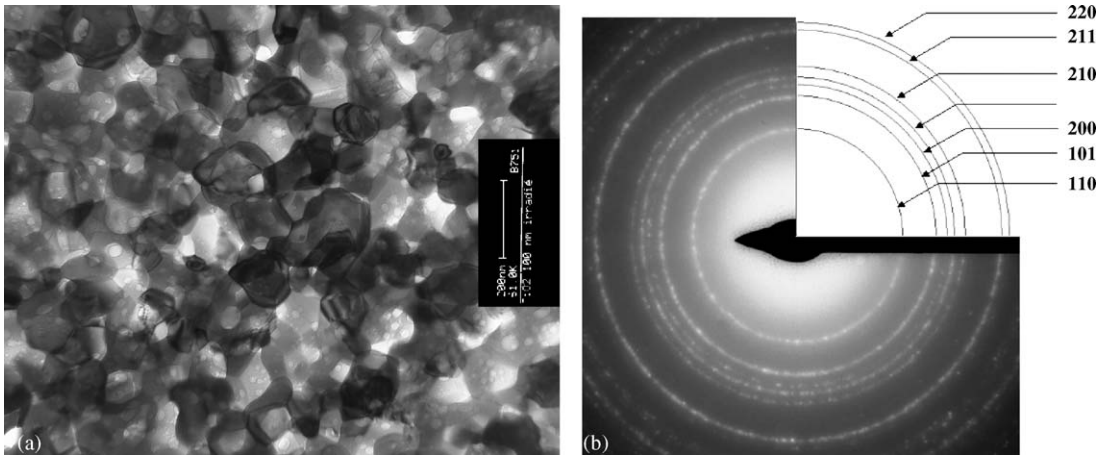

Fig. 1. Electron microscopy and diffraction of the detached TiO_2 films.

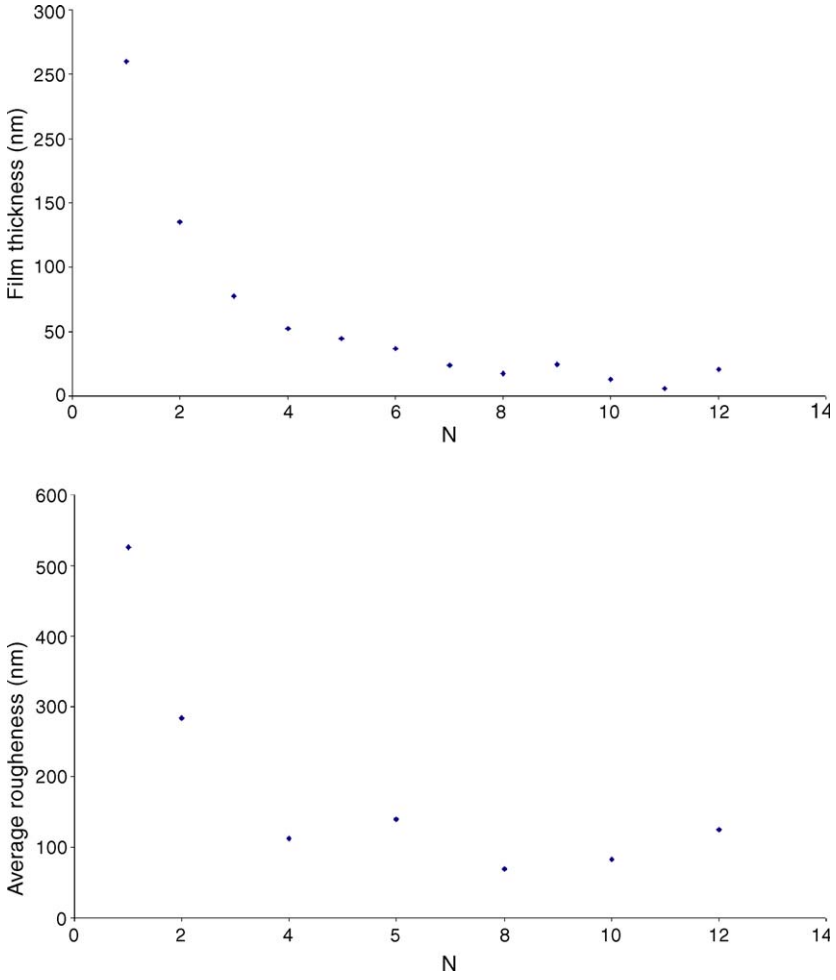

Fig. 2. Variation of film thickness (a) and roughness (b) with the number N of pulses.

case, the opposite is observed, namely the roughness decreases with decreasing h. This rules out the mechanism (c).

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 bandgap, E_g, the main absorption paths couple delocalized states. When $h\nu < E_g$, optical absorption involves either localized states (associated with defects, impurities or the surface) or delocalized surface states. In our case, $h\nu = 5\ \text{eV} > E_g \approx 3\ \text{eV}$.

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 both the light absorption depth, δ, and the mean free path of the electrons are much less than the dimensions of the irradiated sample, laser heating may be viewed as localized at the irradiated surface. The equations governing the depth dependent temperature, T, are now well known. When heating is sufficient, phase transitions (melting, vaporization) may occur. The energy absorbed in the irradiated zone serves to heat it, the substrate and the surrounding atmosphere.

In the case of a film–substrate system, when the thickness of the film cannot be neglected (i.e. the heat diffusion through the interface cannot be neglected), T is given by [5]:

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

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

In these equations, $A = (1 - R)$, 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.

A correct evaluation of the energy effectively provided to transform the sample requires careful calculations of the role of the sample itself. When dealing with processes such as vaporization, it is also necessary to take into account the fact that it is a non-isothermal one, with a strong Arrhenius-type temperature dependence of the evaporation rate constant, R.

In order to evaluate T by means of Eqs. (1a) and (1b), it is necessary to know the values of the optical and thermal properties of the film and the substrate, at high temperature.

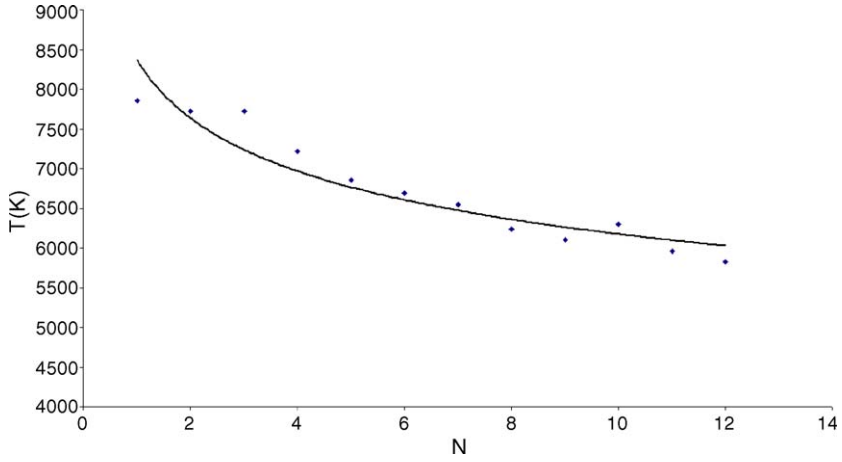

Fig. 3. Variation of the calculated maximum temperature with the number N of pulses.

Unfortunately, these are not known at the highest temperatures calculated in the present work. So, in a first attempt, we choose to follow the following procedure. 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) [7]. The temperature is then evaluated by means of Eqs. (1a) and (1b). The evaporation rate of TiO_2 is calculated by means of the classical thermal rates equations. It turns out that the calculated values are much too high. Therefore, we estimate the value of T required to obtain the experimental value of the ablation rate after the second pulse (as seen by profilometry, the first pulse gives rise to a phase transformation, whose origin will be studied in a further work. So, we assume that the ablation starts at the second pulse). The calculated ablation rates at the other pulses are then multiplied by the same numerical factor. The resulting maximum temperatures during the succeeding pulses are given in Fig. 3. The maximum temperatures versus the film thickness are given in Fig. 4. It turns out that there is a good agreement between the experimental and theoretical results.

From this calculation, the fact that the ablated thickness per pulse decreases with decreasing h (or increasing N) may be due to a negative feedback between heat diffusion and film thickness. Indeed, the thickness of the films compares with the heat diffusion length during the pulses. At high temperature, the heat diffusion length of the substrate is larger than the one of the film. Hence, the heat diffuses through the film and attains the substrate, where it diffuses more rapidly when the film becomes thinner. It is worth noting that the opposite takes place at low temperature, since, under these conditions, the heat diffusion length is larger in the film than in the substrate. From this calculation, we conclude that the mechanism (*d*) may be responsible for our experimental results.

At this stage, we may also rule out the role of the plasma. Indeed, we are working under experimental conditions where the width of the irradiating beam is much larger than the ablated thickness. The plasma results from the interaction between the incoming laser beam and the evaporated species. When h decreases, the ablation rate decreases and also the quantity of the evaporated species. Hence, the energy absorbed in the plasma would decrease, and there would be less screening by the plasma itself, giving rise to more laser energy attaining the film and hence an increased ablation rate, in opposition to the observed facts. It is worth noting that negative feedback by the plasma is mainly observed in high aspect ratio holes, where the

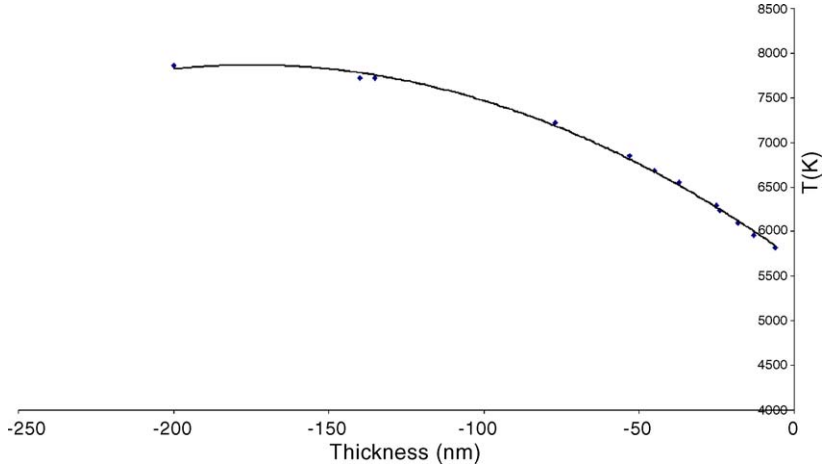

Fig. 4. Variation of the calculated maximum temperature with the film thickness.

width of the beam compares with the ablated thickness. This rules out the mechanism (b).

Let us now examine the possible role of electronic effects. It is known that TiO_2 is a photocatalyst [1]. This means that photoexcited electrons play a role in surface reactions. 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 photo-assisted surface effects, it has been argued [8] that the cohesive properties of electronically excited states are different from the ones of non-excited ones. In the case of covalent bonds, the activation energy for bond breaking is expressed by [8]:

$$E_b = H_b - TS_b \tag{2a}$$

$$H_b = M + U(1 - cn) \tag{2b}$$

where S is the associated entropy. M is a so-called metallic part. U is related to the strength of the covalent bond. n is the electron density associated with one excited covalent bond. n^{-1} is the number of atoms among which the electronic excitation is shared. In other words, it is a measure of the spatial extension of the wavefunction of the excited state. Therefore, for the non-excited state, $E_b = E_b\ (n = 0) = M + U - TS_b\ (n = 0)$. It has been calculated that:

$$\Delta S_b = S_b(n) - S_b(0) = -(3/2)kn^{-1}\ln(1 - cn) > 0 \tag{3}$$

Since H_b and S_b both decrease with increasing n (hence by electronic excitation), E_b may either increase or decrease.

The overall desorption rate also depends on the number of electronically excited states. This is expected to be proportional to the instantaneous fraction of photoexcited electrons, f.

Altogether, the total evaporation rate, R_{tot}, is the sum of the non-excited, R_{ne}, and excited, R_e, contributions:

$$\begin{aligned} R_{tot} &= R_{ne} + R_e \\ &= R_0\left[(1 - f)\exp\left(\frac{S_b(0)}{k}\right)\exp\left(\frac{-H_b(0)}{kT}\right)\right. \\ &\left. + f\exp\left(\frac{S_b(n)}{k}\right)\exp\left(\frac{-H_b(n)}{kT}\right)\right] \\ &= R' + fR'' \end{aligned} \tag{4}$$

Let us assume that the photoexcited sites are characterized by a higher ablation rate than the non-excited ones, i.e. $R'' > R'$. In this case, the higher the number of excited electrons, the higher the ablation rate. The fact that the ablation rate decreases with decreasing film thickness means that the instantaneous number of surface excited sites also decreases. The reason for this may be the following. After optical excitation, electrons and holes recombine and diffuse rapidly. Given the fact that the electron diffusion length is higher than the film thickness, they are distributed quasi-uniformly in the film. When the band gap of the film is narrower than the band gap of the substrate, they remain confined within the film. In this case, it is expected that, at fixed fluence, their surface density increases with decreasing thickness, giving rise to positive feedback effects: the ablation rate increases with decreasing thickness. In our case, the situation is different. Indeed, the band gap of TiO_2 is wider than the one of glass. Hence, diffusing electrons escape through glass. When the thickness of the film decreases, excited electrons attain more rapidly the film/glass interface, where they are transferred into glass. This implies that, at fixed F, their surface density decreases with decreasing film thickness. Therefore, the ablation rate also decreases, as observed experimentally. This implies that the mechanism (e) is, at least qualitatively, compatible with the present experimental results.

Altogether, the previous reasoning indicates that the observed negative feedback between h and the ablation rate of our films may be explained either by the thermal model or by electronic effects or by a combination of both. Although the ''Occam's razor'' principle dictates that the thermal model is the preferred one, more theoretical and experimental work is needed to determine the correct model.

4.2. Detachment of the film

At high F, it turns out that the film detachs from the substrate. This is tentatively explained in the framework of the thermal model. Indeed, at high fluence, the temperature of the film/glass interface is such that the interface stress is very high. When one assumes that the stress is due to the differential thermal expansion of the film and the substrate, it is given by [9]:

$$\sigma_{Thermic} = \left(\frac{E}{1 - \nu}\right)(\alpha_{glass} - \alpha_{TiO_2})\Delta T$$

In this equation, E is the Young modulus of the film, ν the Poisson ratio, α_{glass} the thermal expansion coefficient of glass (it is assumed here that it corresponds to α quartz). One obtains $\sigma_{Thermic}$ = 15.4 GPa, in agreement with other theoretical calculations of film–glass detachment thresholds [10]. It is worth noting that this laser-induced thermal stress might combine with the deposition residual stresses [11]. More work is needed to solve this point.

5. Conclusions

The present work shows that, under KrF excimer laser irradiation, sputter deposited TiO_2 films on glass may be ablated. At low fluence, ''nothing'' occurs (as seen visually and by profilometry). When the fluence increases, one observes a transformation of the system to a thicker and rougher film. This is tentatively associated with the crystallization of the initially amorphous film. When the fluence attains 1.44 J/cm^2, the film detachs abruptly from the substrate. It is worth noting that the detached film presents no sign of melting. In the intermediate regime, when the number of pulses increases, one observes 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 thermal and electronic models are qualitatively compatible with the present experimental

results. Although the ''Occam's razor'' principle dictates that the thermal model is the preferred one, more theoretical and experimental work is needed to determine the correct model. Work is in progress in these directions.

References

[1] U. Diebold, Surf. Sci. Rep. 48 (2003) 53.
[2] T. Le Mercier, J.-M. Mariot, P. Parent, M.-F. Fontaine, C.F. Hague, M. Quarton, Appl. Surf. Sci. 86 (1995) 382.
[3] T.D. Robert, L.D. Laude, V.M. Geskin, R. Lazzaroni, R. Gouttebaron, Thin Solid Films 440 (2003) 268.
[4] Y.-J. Li, T. Matsumoto, N. Gu, M. Komiyama, Appl. Surf. Sci. 237 (2004) 374.
[5] D. Bauerle, Laser Processing and Chemistry, Springer, Berlin, 2000.
[6] E.D. Palik (Ed.), Handbook of Optical Constants of Solids, Academic Press, Orlando, 1985.
[7] R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, 67th ed., CRC Press, Boca Raton, 1986.
[8] M. Wautelet, E.D. Gehain, Semicond. Sci. Technol. 5 (1990) 246.
[9] J.A. Thornton, D.W. Hoffman, Thin Solid Films 171 (1989) 5.
[10] L. Flandin, www.sgm.univ-savoie.fr/cours/ver-cer.pdf.
[11] M.M. Morshed, B.P. Mc Namara, D.C. Cameron, M.S.J. Hashmi, J. Mater. Proc. Technol. 143–144 (2003) 922.