

Titanium Dioxide Thin-Film Deposition on Polymer Substrate by Light Induced Chemical Vapor Deposition

E. Halary-Wagner, F. Wagner, and P. Hoffmann^z

Swiss Federal Institute of Technology Lausanne (EPFL), Advanced Photonics Laboratory, CH-1015 Lausanne, Switzerland

Light induced chemical vapor deposits of titanium dioxide are achieved on poly(methyl methacrylate) substrates from titanium tetraisopropoxide with a long pulse (250 ns) 308 nm XeCl excimer laser, using a mask imaging setup. Similarly to other results obtained on nonpolymeric substrates, localized deposits are achieved in the irradiated area, and the deposited thickness is precisely controlled. This paper focuses on the limitations of the process on polymeric substrates due to laser induced thermal effects. Based both on experimental results and theoretical laser induced temperature rise simulations, the laser induced heating is shown to be responsible for (*i*) the limitation of the used laser fluence to values below 20 mJ cm⁻² pulse⁻¹ so as not to damage the substrate, (*ii*) the appearance of cracks in the deposited films above a certain thickness, and (*iii*) the amorphous state and the 9% carbon contamination of the deposited material which is obtained at the imposed low fluences. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1775931] All rights reserved.

Manuscript submitted October 14, 2003; revised manuscript received February 23, 2004. Available electronically August 11, 2004.

Light induced chemical vapor deposition (LICVD) using excimer lasers in perpendicular irradiation was demonstrated to allow the deposition of titanium dioxide from titanium tetraisopropoxide and oxygen at low substrate temperatures, even room temperature.¹⁻³ However, LICVD on highly temperature-sensitive substrates like polymers are rarely described. Tokita and Okada¹ are, to the best of our knowledge, the only researchers to claim deposition on polymer (polypropylene) substrates, but they did not give any further details on the process. Deposition of titanium dioxide thin films on polymers is of industrial interest for different applications, e.g., optical coatings. Some successful techniques are described in the literature, like sol-gel,⁴ pulsed laser deposition,⁵ radio frequency magnetron sputtering,⁶ reactive ion beam assisted deposition,⁷ and vacuum arc deposition.⁸ LICVD is a very interesting alternative as it allows direct patterning of the deposits and precise control of the deposited thickness, as we already showed on inorganic substrates.^{9,10} In this work, we report the feasibility of LICVD deposition on poly(methyl methacrylate) (PMMA) and evidence the limitations of the technique due to laser induced thermal effects.

Experimental and Theoretical

Deposition techniques.—A precise description of our homemade LICVD reactor was reported elsewhere.⁹ Briefly, a long pulse $(\tau = 250 \text{ ns})$ XeCl excimer laser ($\lambda = 308 \text{ nm}$) irradiates perpendicularly the PMMA substrate placed on a temperature-controlled plate (60°C). Titanium tetraisopropoxide (TTIP, kept in a bubbler at 30°C) is brought in the chamber by an oxygen carrier gas flow (43 standard cubic centimeters per minute (sccm), line temperature: 60°C) while a nitrogen flow (150 sccm) is directed onto the window to prevent deposition on it. The total pressure in the chamber is kept at 10 mbar. A freestanding mask is imaged on the substrate by a single lens. The laser energy per pulse is measured by a pyroelectric detector and regulated by an attenuator. In this process, the deposited thickness is proportional to the number of photons and has an Arrhenius dependence on the substrate temperature. Localized and thickness-controlled multilevel patterns are realized by varying the number of pulses according to Eq. 1, as already described elsewhere. 10

$$e = N \times r_0 \times F \times \exp\left(-\frac{E_a}{RT}\right)$$
$$= t \times f \times r_0 \times F \times \exp\left(-\frac{E_a}{RT}\right)$$
[1]

^z E-mail: Patrik.Hoffmann@epfl.ch

where *e* is the deposited thickness (nm), *N* the number of pulses, r_0 a constant ($r_0 \approx 0.1$ (nm cm² mJ⁻¹ pulse⁻¹), *F* the fluence (mJ cm⁻²), E_a the Arrhenius activation energy ($E_a \approx 21.3 \text{ kJ mol}^{-1}$), *R* the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), *T* the substrate temperature (K), *t* the irradiation time (s), and *f* the laser repetition rate (Hz).

In this work, the deposited thickness is varied from 2 to 250 nm using fluence values between 3 and 15 mJ cm⁻² at a pulse repetition rate of 5 Hz and varying the number of pulses up to 250,000. An example of such a deposit with different steps of different thicknesses is shown in Fig. 1.

Deposit characterization methods.—The deposited thickness (or the ablated depth in the substrate) is measured by profilometry. UVvis transmission spectra through films deposited on PMMA are recorded. Images of the deposits are obtained by optical microscopy combined with a charge-coupled device camera. The chemical composition of the deposits is estimated by X-ray photoelectron spectroscopy (XPS) measurements on an "as-deposited" sample and after ion sputtering (Ar⁺ beam at 2 keV). Raman spectra using a confocal Raman microscope in a backscattered geometry (laser excitation source: 530.9 nm, 100 mW on a 2 μ m diam spot) are recorded to evaluate the crystalline state of the deposited material.



Figure 1. Example of stair-like step deposit obtained on PMMA. Deposition conditions: $F = 8 \text{ mJ cm}^{-2}$, 5000 additional pulses from right to left on each step. The good transparency of the deposit in transmission is evidenced by the structure of the background placed under the polymer sample.



Figure 2. (a) Real temporal shape of laser pulse (measured by photodiode and approximated by linear segments) and (b) temperature rise simulation as function of time and depth for 49.5 nm TiO₂ thick film on PMMA irradiated with single pulse of 10 mJ cm⁻². Each band in contour plot corresponds to 10% of maximum surface temperature rise of 21°C. (3000 depth slices of 1.5 nm and 3,500,000 time slices of 0.2 ps were considered). (c), (d) Temperature depth profiles at different times during and after pulse, extracted from calculations done in (b).

Transmission electron microscopy (TEM) images are realized to determine the nature of the oxide-polymer interface and the oxide film crystallinity.

Laser induced temperature rise modeling.-In addition to the permanent low-temperature heating of the substrate (60°C), each laser pulse induces a temperature rise in the sample for a short time. This temperature rise is a key parameter for understanding the thermal effects undergone by the substrate and the growing film. It can be estimated by solving the one-dimensional heat equation.^{11,12} In this work, a numerical solution described in detail elsewhere¹³ was implemented to model the temperature evolution of a TiO₂ film of given thickness placed on a PMMA substrate and irradiated by a single laser pulse. The real temporal shape of the laser pulse (see Fig. 2a) was used in the calculations, and the coherence length of the light was assumed to be 15 µm. The optical parameters (index of refraction, n, and absorption coefficient, α , at 308 nm) and the thermal parameters (thermal diffusivity, D, and heat capacity, $c_{\rm p}$, with their temperature dependences) considered in the simulations for TiO₂ and PMMA are listed in Table I. Calculations were carried out dividing the sample into 1.5 nm thick depth slices and considering 0.2 ps time slices.

 Table I. Material parameters considered in temperature rise calculations.

	TiO ₂	PMMA
п	3	1.576
α (cm ⁻¹)	4×10^4	4
$\rho (g cm^{-3})$	4.26	1.18
$c_{\rm p} ({\rm J} {\rm g}^{-1} {\rm K}^{-1})$	0.65-1 ^a	1.41 ^b
$D (cm^2 s^{-1})$	0.03-0.005 ^a	0.0011 ^b

^a W.W. Duley, CO₂ Lasers Effects and Applications, Academic Press, San Diego, CA (1976).

^b D. Bäuerle, *Laser Processing and Chemistry*, 2nd ed., Springer, Berlin (1986). An example of the spatiotemporal temperature profile obtained with such a calculation is presented in Fig. 2b (for a 49.5 nm thick TiO_2 film and a 10 mJ cm⁻² fluence). Figures 2c and d show temperature depth profiles at different times after the pulse starts. As discussed in detail later, the film is homogeneously heated, and the heat generated by light absorption in the film diffuses slowly into the substrate.



Figure 3. Laser induced maximum temperature rise for PMMA as function of laser fluence (70,000 slices of 40 nm and 700,000 slices of 0.1 ns taken into account in the calculation).



Figure 4. (a) Ablated depths measured in PMMA after irradiations with 10,000 pulses in presence of TTIP as function of fluence and (b) ablated depth in PMMA in presence of TTIP in different areas irradiated with fluence of 180 mJ cm⁻² and with different numbers of pulses: $N_1 = 5000$, $N_1 + N_2 = 7500$, and $N_1 + N_3 = 12,500$ pulses.

Results and Discussion

Ablation of the polymer in deposition conditions.—Prior to the deposition experiments, ablation of the PMMA substrate is tested in the CVD reactor, in similar conditions to the deposition ones, with and without TTIP.

(*i*) In the absence of TTIP in the chamber, no degradation of the polymer substrate is observed with 2000 pulses in the fluence range tested up to 300 mJ cm⁻². This is in agreement with literature data showing that PMMA is resistant to ablation at 308 nm and requires doping with sensitizers to be ablated.^{14,15} This result is also in agreement with the temperature rise simulations, showing that the laser induced temperature rise for PMMA alone is less than 1°C in this fluence range (see Fig. 3).

(*ii*) In the presence of TTIP in the chamber, the PMMA substrate is already ablated at fluences higher than 20 mJ cm⁻². The ablated depth increases with increasing fluence (see Fig. 4a) and also in-



Figure 5. (a) Calculated maximum surface temperature (\blacksquare) and maximum PMMA-TiO₂ interface temperature (●) as function of TiO₂ film thickness for fluence of 10 mJ cm⁻² and (b) optical microscope images of different thickness step deposit area obtained on PMMA ($F = 5 \text{ mJ cm}^{-2}$) showing appearance of cracks with increasing film thickness.

creases with increasing number of pulses for fluences above this threshold (see Fig. 4b).

These substrate damage tests show that LICVD deposition on PMMA is limited to very low fluence values ($<20 \text{ mJ cm}^{-2}$). Consequently, only a low growth rate per pulse (lower than 1 pm pulse⁻¹) can be obtained, due to the linear dependence of the growth rate on fluence.¹⁶ The ablation of the PMMA substrate in the presence of TTIP in conditions in which PMMA alone is not ablated is due to the formation of an absorbing layer on the polymer which is heated by the laser and heats the polymer. This effect is discussed in the next paragraph, in which the laser induced temperature rise is considered for a thin TiO₂ film on the PMMA substrate.

Appearance of thermal cracks in the deposited film with increasing thickness.—Numerical calculations show that for a given fluence, the laser induced temperature rises at the film surface and at the film-polymer interface and increases with increasing film thickness (see Fig. 5a). This fact can be understood qualitatively by looking at the absorption coefficients listed in Table I. As PMMA is





Figure 6. UV-vis transmission spectra for different TiO₂ film thicknesses deposited with a fluence of $F = 5 \text{ mJ cm}^{-2}$.

almost transparent at 308 nm, the heat is mostly generated by the light absorption in the TiO₂ film. The optical penetration depth l_o of the laser into TiO₂ is $l_o = 1/\alpha = 250$ nm. Therefore, for films thinner than this value, the amount of light absorbed in the film increases remarkably with increasing film thickness. Consequently, the laser induced temperature rise increases with the film thickness. Note also that the film/substrate interface temperature nearly equals the film surface temperature. This effect can be understood by looking at the heat diffusivity values listed in Table I. The average heat diffusivity of TiO₂ is approximately 10 times higher than that of the substrate. As the film thickness is much lower than the heat penetration depth in TiO₂ ($l_T = 2 \times (D\tau)^{0.5} = 1.3 \,\mu$ m), the temperature distribution is nearly homogeneous throughout the film thickness.

Figure 8. Raman spectrum of a selected sample (film thickness: 250 nm, $F = 5 \text{ mJ cm}^{-2}$), compared with the PMMA substrate spectrum. Expected positions of the TiO₂ crystalline peaks are indicated (A stands for anatase and R for rutile).

The low thermal diffusivity of PMMA compared to TiO_2 also explains why the laser induced temperature rise in the film is higher than the one obtained on bulk TiO_2 .

Experimentally, deposition on PMMA is possible for fluences below 20 mJ cm⁻², where the temperature at the film/substrate interface is lower than the thermal degradation temperature of the polymer for any film thickness. TEM cross sections (Fig. 9) show a well-defined interface between the substrate and the film, *i.e.*, no melting is detected at the interface. However, cracks appear in the TiO₂ film above a certain thickness (see Fig. 5b). Based on the laser induced temperature rise simulations, these cracks are believed to originate from thermal dilatation effects.

Physicochemical properties of the deposited material.—The deposited material exhibits a good transparency for visible light, as



Figure 7. XPS analyses on a selected sample (film thickness = 100 nm and $F = 5 \text{ mJ cm}^{-2}$). (a) Ti (2p) region, (b) O (1s) region, (c) C (1s) region, and (d) atomic concentration depth profile.



Figure 9. TEM cross sections of a deposit ($F = 5 \text{ mJ cm}^{-2}$, film thickness: 100 nm). (a) Overview showing homogeneous film thickness and (b) highresolution TEM image of PMMA/TiO2-interface confirming the absence of any crystallinity and of PMMA melting.

shown by the transmission curves in Fig. 6. The positions of the minima (λ_{min}) and maxima (λ_{max}) of the transmission curves (which are due to interferences) enable one to estimate roughly the index of refraction n of the deposited material of thickness e from Eq. 2:

$$\lambda_{\min} = \frac{2en}{p}$$
 and $\lambda_{\max} = \frac{4en}{p}$ [2]

where p is the interference order. $n = 2.1 \pm 0.4$ is found.

XPS analyses of a selected sample are presented in Fig. 7. After calibration of the spectra with respect to the carbon C (1s) peak at 285 eV, the expected positions are found on the as-deposited sample for the Ti (2p 3/2), Ti (2p 1/2) and O (1s) peaks at, respectively 458.6, 464, and 530 eV.¹⁷ The additional O (1s) peaks at, re around 532 eV is characteristic for adsorbed contamination.¹⁷ After sputtering, the Ti 2p peaks are highly broadened, exhibiting large shoulders between 452 and 458 eV, which are typical for the TiO_2 reduction effect under ion bombardment.¹⁷ After removal of the surface contamination layer, the depth profile of atomic concentrations in the bulk (Fig. 7d) shows an average chemical composition of Ti: $30.6 \pm 1\%$, O: 60.8 $\pm 1.1\%$, and C: 8.6 $\pm 1.5\%$. This proves that stoichiometric TiO2 is obtained with an additional 9% of carbon contamination.

Raman spectra of a deposited film on PMMA (see Fig. 8) exhibit no peaks other than those of the substrate, which is characteristic for an amorphous material.¹⁸ This amorphous structure is confirmed by the absence of any crystallites in the high-resolution cross-sectional TEM image (Fig. 9b).

When deposition is carried out at higher fluences on nonpolymeric substrates, no carbon contamination is detected, and at a given surface temperature, the crystalline state changes from amorphous to anatase to rutile with increasing fluence.¹⁹ This annealing-like modification is attributed to the laser induced temperature rise. For the PMMA substrate, it is impossible to use the required fluences for crystalline deposition, because of the low damage threshold. Thus, LICVD deposition on PMMA is limited to amorphous material deposition with the system used here. However, if the deposited film thickness exceeds the heat penetration depth ($l_{\rm T} = 1.3 \,\mu{\rm m}$), it may be possible to crystallize the upper part of the film by irradiating with a higher fluence, without damaging the substrate.

Conclusions

The deposition of localized and thickness-controlled thin films of titanium dioxide on PMMA is demonstrated. Due to the laser light absorption in the film, a nonnegligible temperature rise is generated by the irradiation, which limits the usable range of fluence to values below 20 mJ cm⁻², so as not to damage the substrate. At these low fluences, the film/polymer interface is well defined, exhibiting no evidence of polymer degradation. However, only amorphous films are obtained with additional carbon contamination of 9%. Additionally, some cracks appear in the films when the thickness exceeds a certain value, which is attributed to thermal mismatch effects at the interface. Similar results have been obtained with polycarbonate, poly(ethylene terephthalate) and polyimide substrates.

Acknowledgments

The authors thank Nicolas Xanthopoulos of the Swiss Federal Institute of Technology (EPFL) for the XPS measurements, Thomas Lippert (PSI, Villigen) and Giacomo Benvenuti (EPFL) for the Raman microscopy, and Danièle Laub (EPFL) and Philippe Buffat (EPFL) for the TEM analysis. The project was funded by the Swiss National Science Foundation under project no. 20-59404.99.

The Swiss Federal Institute of Technology Lausanne (EPFL) assisted in meeting the publication costs of this article.

List of Symbols

- heat capacity, J $g^{-1}\ K^{-1}$
- $C_{\rm p}$ Dthermal diffusivity, cm² s⁻¹
- film thickness nm
- Arrhenius activation energy, kJ mol-1 E_{a}
- laser repetition rate, Hz
- F laser fluence on the substrate, mJ cm⁻² pulse⁻¹
- optical penetration depth $(=\alpha^{-1})$ l_{0}
- heat penetration depth, µm $l_{\rm T}$
- refractive index п
- Ν number of pulses
- р interference order
- a constant r_0
- Ř gas constant, $(8.314 \text{ J mol}^{-1} \text{ K}^{-1})$ irradiation time, s

Greek

- optical absorption coefficient, cm⁻¹ α
- laser wavelength, nm λ
- wavelength of a minimum in the transmission curve
- λ_{min} wavelength of a maximum in the transmission curve
- λ_{max} laser pulse duration, ns

References

- 1. K. Tokita and F. Okada, J. Appl. Phys., 80, 7073 (1996).
- E. Halary, G. Benvenuti, F. Wagner, and P. Hoffmann, Appl. Surf. Sci., 154/155, 2. 146 (2000).
- A. Watanabe, T. Tsuchiva, and Y. Imai, Thin Solid Films, 406, 132 (2002).
- 4. M. Langlet, A. Kim, M. Audier, C. Guillard, and J. M. Herrmann, Thin Solid Films, 429, 13 (2003).

- 5. N. Lobstein, E. Millon, A. Hachimi, J. F. Muller, M. Alnot, and J. J. Ehrhardt, Appl. Surf. Sci., 89, 307 (1995).
- 6. S. Ben Amor, G. Baud, M. Jacquet, and N. Pichon, Surf. Coat. Technol., 102, 63 (1998)
- 7. Z. Ding, X. Hu, G. Q. Lu, P.-L. Yue, and P. F. Greenfield, Langmuir, 16, 6216 (2000).
- 8. B. Straumal, N. Vershinin, K. Filonov, R. Dimitriou, and W. Gust, Thin Solid Films, 351, 204 (1999).
- 9. E. Halary-Wagner, P. Lambelet, G. Benvenuti, and P. Hoffmann, J. Phys. IV, 11, Pr3 (2001).10. E. Halary-Wagner, T. Bret, and P. Hoffmann, Appl. Surf. Sci., 208-209, 663 (2003).
- 11. Laser Processing and Chemistry, 2nd ed., D. Bäuerle, Editor, Springer, Berlin (1996).
- 12. P. Baeri and U. Campisano, in Laser Annealing of Semi-Conductors, J. M. Poate

- and J. M. Mayer, Editors, Academic Press, New York (1982).
- 13. E. Wagner, Ph.D. Thesis 2650, EPFL, Lausanne, Switzerland (2003).
- 14. T. Lippert, R. L. Webb, S. C. Langford, and J. T. Dickinson, J. Appl. Phys., 85, 1838 (1999).
- 15. R. L. Webb, S. C. Langford, J. T. Dickinson, and T. K. Lippert, Appl. Surf. Sci., 127-129, 815 (1998).
- 16. E. Halary-Wagner, T. Bret, and P. Hoffmann, Adv. Mater. CVD, Accepted for publication.
- F. Zhang, S. Jin, Y. Mao, Z. Zheng, Y. Chen, and X. Liu, *Thin Solid Films*, 310, 29 (1997).
- 18. L. Escobar-Alarcon, E. Haro-Poniatowski, M. A. Camacho-Lopez, M. Fernandez-
- Guasti, J. Jimenez-Jarquin, and A. Sanchez-Pineda, *Appl. Surf. Sci.*, 137, 38 (1999).
 E. Halary-Wagner, F. Wagner, A. Brioude, J. Mugnier, and P. Hoffmann, *Adv. Mater. CVD*, Accepted for publication.