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

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Light Induced Chemical Vapor Deposition (LICVD) using Excimer lasers in perpendicular irradiation was demonstrated to allow for deposition of titanium dioxide from titanium tetra-isopropoxide and oxygen at substrate temperatures down to room temperature (1, 2).

Projection image LICVD allows direct patterning of the deposits and precise control of the deposited thickness, as we already showed on inorganic substrates (3, 4).

In this work, we report on the feasibility of LICVD deposition on PMMA and evidence the limitation of the technique due to thermal effects.

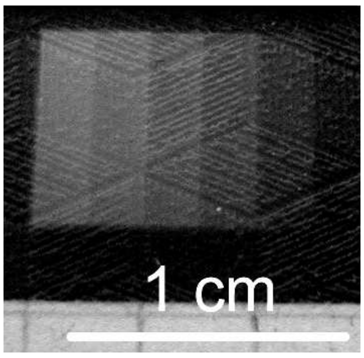

Fig. 1 - Example of stair step deposits obtained on PMMA. Dep. conditions: F=8 mJ/cm^2, 5000 additional pulses from right to left on each step. The high transparency of the deposits is proven by the visibility of the background structure

Due to the laser light absorption in the high index of refraction film (n=2.6±0.4 , estimated from transmission spectra see Fig. 4), a non-negligible temperature rise is generated by the irradiation, which limits the usable range of fluence to values below 20 mJ/cm^2, in order not to damage the substrate. This experimental limit is confirmed by theoretical modeling. An example of the temperature contour map induced by one laser pulse is shown in Fig. 2. At these low fluences, the film/polymer interface is well defined, exhibiting no evidence of polymer degradation (see Fig. 6).

However, only amorphous films according to Raman and TEM results (see Fig. 6 b) are obtained with additional carbon contamination of 9% (see Fig. 5). The highly transparent films (see Figs. 1 and 4) show good adherence, as confirmed by scotch tape test. Some cracks appear in the films when the thickness exceeds about 50 nm, which is attributed to thermal mismatch effects at the interface.

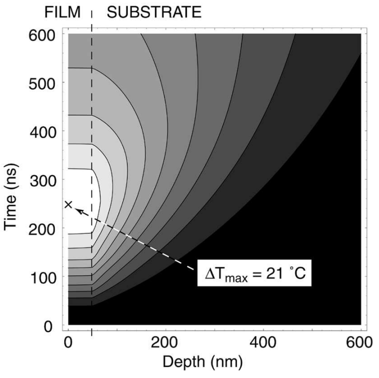

Fig. 2- Temperature rise simulation as function of time and depth for a 49.5 nm TiO$_2$ thick film on PMMA irradiated with a single pulse of 10 mJ/cm^2. Contour lines correspond to 10% of the max. surface T rise of 21°C.

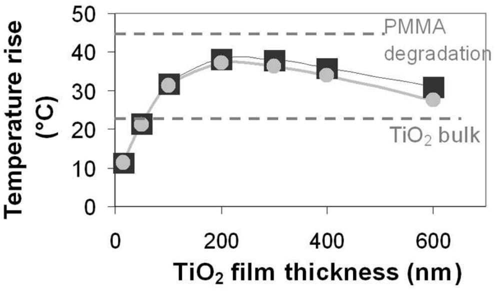

Fig. 3 - Calculated maximum surface temperature (squares) and maximum PMMA-TiO$_2$ interface temperature (gray circles) as function of TiO$_2$ film thickness, for a fluence of 10 mJ/cm^2.

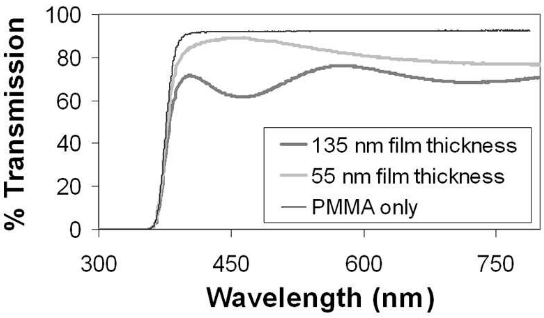

Fig. 4- UV-vis transmission spectra for different TiO$_2$ film thicknesses, deposited with a fluence of F=5 mJ/cm^2.

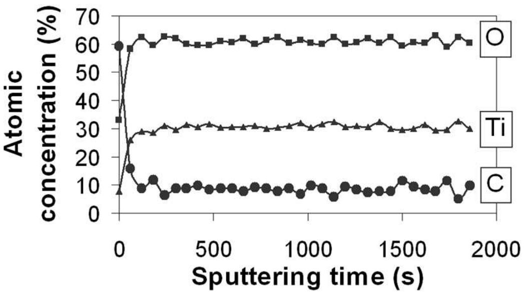

Fig. 5- XPS analyses on a selected sample (Film thickness = 100 nm and F=5 mJ/cm^2) atomic concentration depth profile of Ti, O, and C.

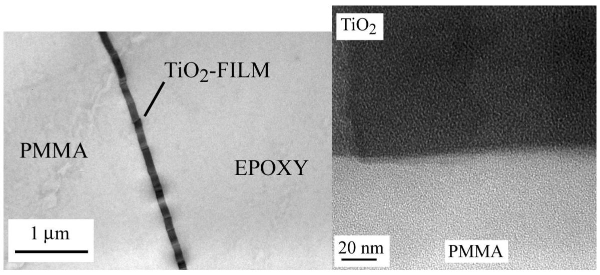

Fig. 6- TEM cross sections of a deposit. a) Overview showing the homogeneous film thickness and b) High resolution TEM image of the PMMA/TiO$_2$-interface confirming the absence of any crystallinity.

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