

Matrix Assisted Pulsed Laser Deposition of light emitting polymer thin films with very low roughness

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Matrix-Assisted Pulsed Laser Evaporation (MAPLE) technique is a non-destructive laser-based approach particularly suitable for depositing organic materials, even with complex chemical structures, including bio-organic molecules, coordination compounds and polymers [1]. The main advantages of MAPLE approach are the precise control of thickness and the ability to deposit multilayers and patterned films at controlled growth. In our work, we have deposited MAPLE-films of green-light emitting polymer poly[9,9-dioctylfluorenylene-2,7-diyl]-co-(1,4-diphenylene-vinylene-2-methoxy-5-2{-ethylhexyloxy} on SiO₂-ITO substrates benzene)], [ADS 125 GE, (Sigma-Aldrich)]. The deposited films properties have been tested as function of polymer concentration (C), target-substrate distance (d_{TS}) and substrate rotation speed (ω). Experimental results demonstrate that a good interplay among the deposition parameters makes possible to deposit very flat (9nm-rough) polymeric layer with a thickness (40nm) compatible with photonic applications. To form the MAPLE-target, the polymer was dissolved in toluene with three different weight concentration C of 0.30, 0.15 and 0.03wt% and then filtrate. The obtained solutions were frozen at the liquid N₂ temperature and mounted on a refrigerated target-holder within a vacuum chamber evacuated down to the pressure of $5 \times 10^{-4} Pa$) before each deposition. A KrF excimer laser-LambdaPhysik (LPX-305i)-beam ($\lambda=248nm$; $p=20ns$) was focused on the target surface, at the repetition rate of 10Hz and with angle of 45° with respect to the target normal. A fluence value of $250mJ/cm^2$ was set in all the depositions. The target was rotated at the frequency of 3Hz to allow uniform erosion and its temperature was kept constant (77K) during the deposition. The substrate was placed at 3, 4.5 or 6cm in front of the target. Target-substrate distance was considered as a working parameter

because it is expected to influence the amount of residual solvent reaching the substrate as well as chain conformation and entanglement. We tested the influence of substrate rotation based on the working principle of the spin-coating technique [2] that exploits the dependence of the solvent evaporation rate on the substrate rotation speed to favour film drying. A spin-coated film was deposited by a solution of the polymer in toluene with weight concentration of 0.15wt%. The film morphology was investigated by AFM Park instrument (XE-100). The absorbance UV-Vis spectra are recorded by a Cary-5000-Varian spectrophotometer instrument, while the luminescence spectra are carried out by a Cary-Eclipse Varian fluoremeter. AFM topography-analyses of the deposited samples show a decrease in the average roughness as the target-substrate distance increases; AFM images show topography consisting of globule-like features with reduced height and more sharp tops as d_{TS} increases from 3 to 6cm. In particular, doubling d_{TS} resulted in reducing the roughness of about 9%, 16% and 38% on scanned area of $30 \times 30\mu m^2$, $10 \times 10\mu m^2$ and $5 \times 5\mu m^2$ respectively. Since fixing $d_{TS}=6cm$ gave the lowest recorded roughness value, the polymer was further deposited at such d_{TS} with decreasing weight percentages. As expected from molecular dynamic simulations [3], this parameter was effective in reducing the globule-like surface feature dimension and film roughness: halving the polymer concentration from 0.3wt% to 0.15wt% the roughness was reduced of about 72%, 66% and 54% on scanned area of $30 \times 30\mu m^2$, $10 \times 10\mu m^2$ and $5 \times 5\mu m^2$ respectively (Fig.2). A further decrease in polymer concentration was such to let very thin film thickness and to make dominant the effect of the solvent. In fact, circular-like surface features, characteristic of the MAPLE deposits, can be observed only at the lowest sampled polymer concentration (0.03wt%). As regards substrate rotation during

the MAPLE-deposition, from the AFM images it results that at polymer concentration of 0.3wt% and $d_{TS}=3cm$ substrate rotation decreases the roughness and favors smaller globules, while it seems to have less influence at $d_{TS}=6cm$ since, in this case, the roughness is approximately the same for either rotated or un-rotated substrate. This confirms that most of the solvent is already evaporated at $d_{TS}=6cm$. In fact substrate rotation should help solvent evaporation, like in spin coating experiments, and so modify the surface morphology together with the film roughness. At lower distances ($d_{TS}=3cm$) larger amount of residual solvent reaches the substrate and during solvent evaporation, the deposit viscosity changes addressing the kinetics of the film morphology evolution by the diffusion ability of the polymer chains depending on the local concentration. At this distance the substrate rotation induced a reduction of film roughness. By evaluating the absorption and emission properties of the films deposited under different experimental conditions, we have found very similar emission properties with an emission band peaked at $525nm$ (Fig.1) indicating that from optical point of view no significant change in the electronic properties occurs for the different deposition conditions. This is important in order to guarantee that the MAPLE is a not-invasive deposition technique, as the polymer-laser interaction is not effective in changing the emission properties through relevant photo-chemical or photo-thermal damages. In contrast, the examined deposition parameters were found to influence/tune the thickness and morphology characteristics (average roughness and topography) of the deposited films.

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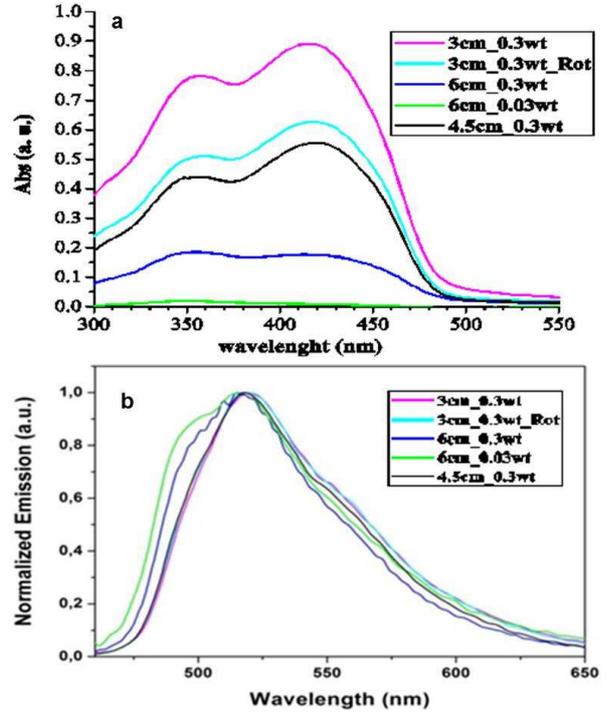


Figure 1. a Absorption and b emission spectra of the MAPLE-deposited film.

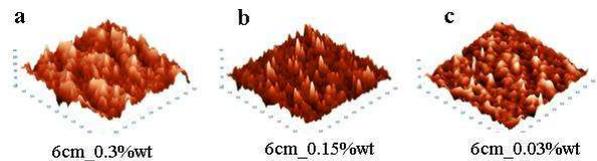


Figure 2. 3D AFM topography images acquired over a $5 \times 5 \mu m^2$ -large scan area of the MAPLE samples deposited at a $d_{TS}=6cm$ and at different concentration.