MAPLE deposition of nanoparticles and polymer films

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Matrix Assisted Pulsed Laser Evaporation (MAPLE) is a recently developed laser-based technique, which derives from the PLD. It represents an efficient method for the deposition of polymer and biomaterial films. In fact, MAPLE offers a gentle mechanism to vaporize high molecular weight organic materials without laser induced damage and, in principle, with a good thickness control of the deposited films, thanks to the pulsed nature of the process. In this technique, the organic material is diluted in a volatile noninteracting solvent, with concentration of a few percent (in weight), and frozen at the liquid nitrogen temperature. The frozen target is irradiated with a pulsed laser beam at low laser fluence (energy density at the laser spot on the target) values $(50-500 \text{ mJ/cm}^2)$. The laser energy is mainly absorbed by the solvent and converted into thermal energy, allowing the solvent to vaporize. The solute molecules receive enough kinetic energy through collective collisions with the molecules of the evaporating solvent to be transferred in the gas phase and to be deposited on a nearby substrate. The solvent is pumped away, so, the deposited film is completely formed by the solute material.

MAPLE has been successfully used to deposit thin films of:

- a) Methoxy Ge Triphenylcorrole (Ge(TPC)OCH3) Films of this polymer were deposited by MAPLE. Their good quality was confirmed by AFM investigations and by the study of their optical properties. The absorption and photoluminescence properties of the deposited film were investigated, showing the same properties of the solution. The Soret and Q bands were preserved after the laser transfer process, with only a slight shift due to a probable formation of aggregates during the film growth of the polymer. The peaks in the spectra of the spin coated film presented higher shift and broadening in comparison with the film deposited by MAPLE, suggesting a higher presence of aggregates.
- b) Poly(9.9-dioctylfluorene) polymer PFO thin films were deposited by MAPLE using a KrF excimer laser. The influence of the laser fluence $(50-500 \text{ mJ/cm}^2)$ and the nature of the solvent (chloroform, toluene, tetrahydrofuran) on the films properties have been studied. The chemical composition of the deposited films was investigated by Fourier transform infrared (FTIR) spectroscopy and compared with the one of spin coated films. To investigate the effect of the deposition parameters on the optical properties of the films, photoluminescence (PL) measurements were performed. Poor structural and optical properties were observed for films deposited starting from chloroform solutions. In contrast, when using toluene as solvent, the spectra characteristics improved with increasing laser fluence. The characteristic emission bands of the PFO polymer were nicely detected for films deposited starting from a tetrahydrofuran (THF) solution. Moreover, in this last case, the PF8 structure is preserved at high laser fluences, too.
- c) Nanoparticles thin films The MAPLE technique was exploited for the deposition of titania (TiO_2) nanoparticle thin films to be used for gas sensor applications. For this purpose, an aqueous solution of TiO₂ nanoparticles, synthesized by a novel chemical route, was frozen at the liquid nitrogen temperature and introduced in a vacuum chamber to be irradiated with a pulsed ArF excimer laser. The volatile solvent was pumped away while the TiO_2 nanoparticles were deposited on Si and Al₂O₃ substrates. A uniform distribution of TiO_2 nanoparticles with an average size of about 10 nm was obtained, as demonstrated by high resolution scanning electron microscopy (SEM-FEG) inspection. We realized gas-sensing devices based on resistive transduction mechanism by using the TiO_2 nanoparticles thin films deposited by the MAPLE technique onto suitable rough alumina substrates equipped with interdigi-

tated electrical contacts (IDC) and heating elements. Electrical characterization measurements were carried out in controlled environments. Typical gas sensor parameters (gas responses, response/recovery time, sensitivity, and low detection limit) towards low concentrations (20-200 ppm) of ethanol and acetone were measured. The results of the gas-sensing tests are very promising.