

MATRIX ASSISTED PULSED LASER EVAPORATION FOR TiO₂ NANOPARTICLE THIN FILM DEPOSITION

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The Matrix Assisted Pulsed Laser Evaporation (MAPLE) technique has been used, for the first time, for the successful deposition of titania (TiO₂) nanostructured thin films. An aqueous solution (20% wt) of colloidal TiO₂ nanoparticles with anatase phase, synthesized by a novel chemical route, was frozen and then irradiated with a pulsed ArF excimer laser ($\lambda=193$ nm, $\tau=20$ ns). The nanoparticles were deposited on (100) Si substrates. A uniform and compact distribution of TiO₂ nanoparticles forming a continuous film was obtained, as demonstrated by high resolution Scanning Electron Microscopy (SEM-FEG) inspection. Randomly distributed spherical particles with an average diameter of 200 nm were also observed on the film. A comparison with a spin coated thin film obtained from the same starting solution allowed to better evaluate the effects of the laser deposition process. Energy Dispersive X-ray Spectroscopy (EDX) revealed the presence of only the titanium and oxygen signals, and X-Ray Diffraction (XRD) spectra demonstrated that the anatase phase and nanoparticle dimensions were preserved. Our results are very interesting for the development of technological devices like sensors.

Keywords: MAPLE, Excimer laser, thin films, TiO₂ nanoparticles, Spin-coating

1. Introduction

Nanoparticles-based materials have attracted much attention in recent years because of their characteristic size- and geometry dependent chemical and physical properties [1]. High quality nanoparticles can be deposited by different deposition techniques like Sol-Gel, Molecular Beam Epitaxy (MBE), Metal-Organic Chemical Vapour Deposition (MOCVD) and Pulsed Laser Deposition (PLD) [2-6]. However, despite the good quality of the nanoparticles deposited with these techniques, they are usually embedded in semiconductor or dielectric layers directly in their final position, thus preventing their transfer onto planar substrates and their mixing with other materials. Moreover, when deposited as thin films they present a quite large dimension distribution function. More recently, nanoparticles with quite controlled dimensions and very narrow size dispersion have been obtained by colloidal growth techniques, which are relatively easy and cheap [7,8]. Colloidal nanoparticles offer a greater versatility since they can be incorporated into polymer and glass matrices and into different photonic structures. Starting from the solution, these nanoparticles can also be deposited as thin films, typically by using spin coating and drop casting techniques. These deposition methods are quite simple and not expensive but they do not ensure a good control of the film thickness and uniformity.

The Matrix Assisted Pulsed Laser Evaporation (MAPLE) is a new laser-based deposition technique, which derives by the Pulsed Laser Deposition (PLD). This technique is emerging for polymers and biomaterials deposition, since it provides a gentle mechanism to transfer small and large molecular weight species from condensed phase into the vapour phase. In this technique the

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organic or nanosized material is diluted in a volatile non-interacting 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, whose energy is principally absorbed by the solvent and converted to thermal energy, allowing the solvent to vaporize and to be evacuated by the vacuum system. The solute material collects on a suitable substrate placed in front of target. Different materials have been deposited by this technique, like optical active polymers, proteins, bacteria, and DNA [9].

The working principle of the MAPLE technique can be exploited for the deposition of colloidal nanoparticles to be employed e.g. in gas sensor devices. In fact, the nanoparticle solution, once frozen in liquid nitrogen, can be used as target to be laser-irradiated in the MAPLE technique to produce a nanoparticle film. In this way, all the advantages (small dimensions with low size dispersion) offered by these nanostructures can be preserved and exploited.

The MAPLE technique was patented [10] for the deposition of composite layers of non-electrically-conducting polymers and electrically conducting particles. Moreover, MAPLE deposition of carbon nanotubes is reported too [11].

To our knowledge, nanoparticles deposition using the MAPLE technique was not previously tried.

In this paper we report on the deposition by MAPLE of thin films of TiO₂ colloidal nanoparticles prepared by a well established chemical route [12]. The versatility of the properties and applications of TiO₂ nanoparticle thin films are documented by the recent literature [13-15]. Our method can represent a great advance for the improvement of the quality of nanoparticle thin films thanks to the possibility of exploiting the colloidal nanoparticle proprieties in a laser based deposition method, thus widening the application of these systems in different technological fields.

2. Experimental details

TiO₂ nanocrystals were prepared by using the following procedure: 1 ml of Ti(IV) *tert*-butoxide, was added to benzyl alcohol (5 ml). The reaction mixture was transferred into a pyrex tube and heated in a furnace at 220 °C for 2 days. The resulting milky suspensions were centrifuged, the precipitates thoroughly washed in ethanol and dichloromethane, and subsequently dried in air at 60 °C.

X-Ray Diffraction (XRD) was used to verify the structure of the synthesised nanoparticles. The diffraction patterns were obtained with a powder diffractometer PHILIPS, Mod.P1729, by using the Cu K α line, filtered with a normal θ -2 θ geometry. The spectra were recorded in the interval 20-70° with a step of 0.02°.

Successively, the nanoparticles were diluted in deionised water with a concentration of 20% wt and put in ultrasonic bath for 10 minutes to prevent from aggregation. The solution was gradually immersed in liquid nitrogen (-196 °C) and quickly mounted inside the vacuum chamber evacuated down to few Pa by a scroll pump. This target was irradiated with an ArF ($\lambda=193$ nm) excimer laser (Lambda Physik LPX-305i) with pulse duration of 20 ns and repetition rate of 10 Hz. The laser beam was attenuated and focused (with a rectangular spot of 0.075 cm²) to obtain an energy density of 550 mJ/cm². The number of subsequent laser pulses, applied to deposit the film, was 16000. Before deposition, 400 pulses were used in order to remove the superficial layer of frozen aqueous vapor formed on target, while a shutter screened the substrate.

The solvent evaporation process allowed the nanoparticles to deposit on <100> single crystalline Si substrate placed at 30 mm in front of the target which rotated with a frequency of 3 Hz to allow a uniform erosion. A rise in pressure resulted during deposition to a maximum value of 12.5 Pa due to evaporation of the volatile solvent.

The same starting solution, ultrasonically treated, was spin coated to deposit a TiO₂ nanoparticle thin film for comparison.

The morphology of the films was investigated by using a GEMINI Field Emission Scanning Electron Microscope (SEM-FEG) equipped with both in-camera ET and in-lens secondary electron detectors and with an in-lens backscattered electrons detector. Element identification and structure information were obtained by Energy Dispersive X-ray Spectroscopy (EDX) and XRD. A JEOL instrument was used for EDX spectra. Glancing incident X-Ray Diffraction analysis was performed on the films to confirm the TiO₂ nanoparticles anatase phase

by using a high-resolution x-ray diffractometer (HRD3000 Ital Structures) in parallel beam optic configuration (Max-Flux™ Optical System) with a glancing angle of 1°.

3. Results and discussion

The XRD spectrum of the TiO₂ nanoparticles before laser irradiation is reported in the main panel of Fig. 1. The position of the x-ray peaks, labeled in the figure, was consistent with the anatase phase (ICDD).

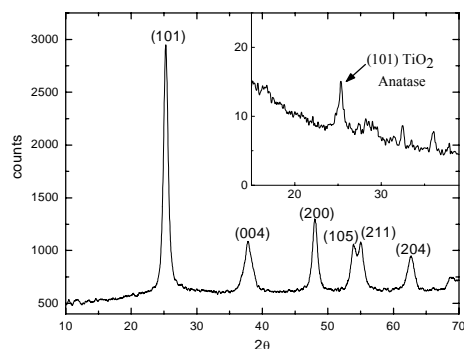


Fig. 1. XRD spectra obtained from TiO₂ nanoparticles as synthesized (main panel) and as thin film deposited by MAPLE (inset).

The characteristic line broadening of the diffraction peaks clearly points out the nanocrystalline domain. The average particle size, as estimated by using the Debye-Scherrer formula, is (11 ± 1) nm for the (101) and (200) peaks, and (6.7 ± 0.5) nm for the (004) peak. These two different values can be related to an anisotropic growth along different crystallographic directions, which can result in faceting. The phase and size of the TiO₂ nanoparticles were preserved during the MAPLE transfer from the target to the silicon substrate, as evidenced by the XRD spectrum in the inset of Fig. 1. The main peak of the anatase phase is visible, whose width corresponds to an average crystalline size of about 10 nm, in agreement with the value obtained from the same peak in the main panel.

A series of SEM micrographs obtained from both the spin coating and MAPLE films is reported in Fig. 2. In particular Figs. 2 a) and b) compare the morphology of the films at lower magnification, allowing an inspection of the overall features: the spin coating film consists of nanoparticle agglomerates, randomly scattered on the substrate, whereas the MAPLE film shows two main features, i.e. a uniform coverage of TiO₂ nanoparticles having a mosaic-like structure, and a distribution of spherical particles with a diameter ranging from tens to hundreds of nanometers. The high resolution images of the same films are shown in Figs. 2 c) and 2 d).

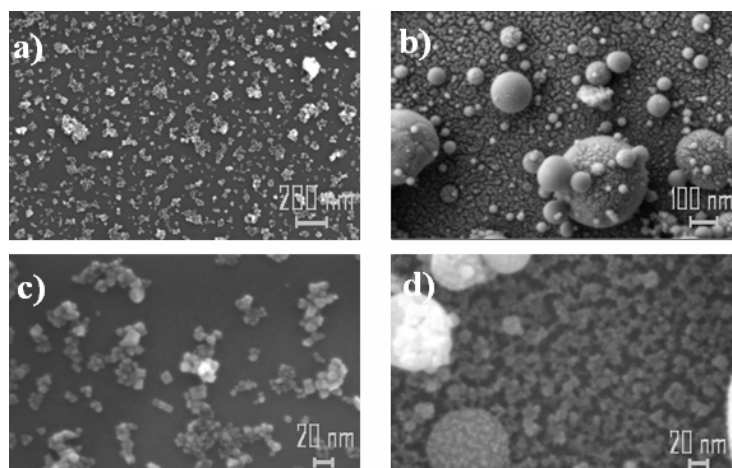


Fig. 2. Low (a,b) and high (c,d) magnification SEM micrographs of spin coated (a,c) and MAPLE (b,d) deposited TiO₂ nanoparticle films.

It is worth noting that in the high resolution mode it is possible to distinguish in the spin coating film the single nanoparticles forming the agglomerates. Most important, two families of nanoparticles can be noted: spherical nanoparticles with an average diameter less than 10 nm (in agreement with the XRD analyses) and bigger faceted particles, showing squared edges, with typical sizes of a few tens on nanometers. These TiO₂ nano-boxes, reflecting the tetragonal structure of the anatase phase, can be the result of anisotropic growth, already suggested by the X-ray analyses. The high resolution image of the MAPLE film suggests the formation on the substrate of a layer of nanoparticles, which are not singularly distinguishable, as in the case of the spin coating film. This could be a particle superposition effect, also suggested by the surface morphology of the spherical particles, present in the film. Some of these particles show a coverage on their surface, whose morphology is similar to that observed on the substrate. This indicates a time dependent process during which nano and spherical particles reach the substrate at different times, forming a layer consisting of a continuous film of nanoparticles plus nanoparticle-covered and uncovered spheres. The formation of spherical structures is peculiar of the MAPLE deposited films and deserves further discussion. Titania spherodization has been observed in the literature¹⁶ after plasma treatment of titania powder. The presence of such microstructures suggests that similar mechanisms can occur during the MAPLE process, due to the concurrence of different effects, as discussed afterwards. In order to exclude the possibility of a different origin of these spherical particles, EDX analysis were also performed; different x-ray spectra were collected by focusing the electron beam of an EDX-equipped SEM on the film and on the bigger particles. In both cases the titanium and oxygen signals were detected, together with the signal coming from the silicon substrate due to the small thickness of the film (Fig. 3).

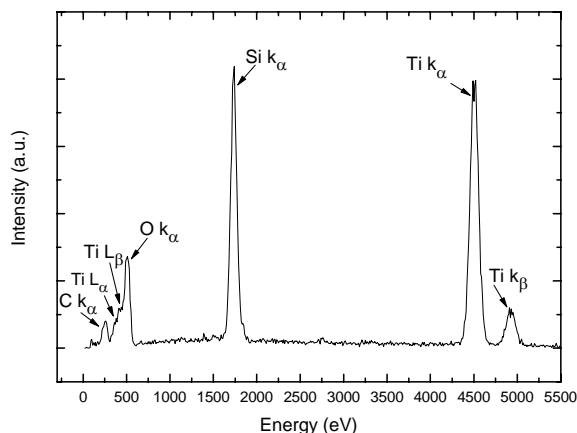


Fig. 3. EDX spectrum obtained from a thin film of TiO₂ nanoparticles deposited by MAPLE.

The realization of the compact uniform layer of TiO₂ nanoparticles is a very interesting result obtained by the MAPLE technique. However, unwanted microscopic structures are present on the film surface. The presence of these structures can be due to several concurring factors. First, the starting vacuum conditions were not optimal because a quite high background pressure (a few Pa) was obtained by using the scroll pump. This high pressure could agglomerate the evaporated nanoparticles depositing on the Si substrate. Moreover, the target to substrate distance (30 mm) was small to reduce the number of such structures. Finally the target temperature did not remain constant over the entire thickness during the evaporation process.

4. Conclusions

In conclusions, the new MAPLE technique has been successfully adapted to deposit anatase TiO₂ nanoparticles thin films. A TiO₂ thin film was deposited for comparison by the spin-coating technique. Compared to the latter film, the one deposited by MAPLE presents a more uniform and compact distribution of TiO₂ nanoparticles of about 10 nm in diameter. Microscopic structures are present on the film surface probably due to the fast evaporation of the solvent which

causes the spherical aggregation of the nanoparticles. Further experiments are in progress to avoid these features. Electrical characterizations to test the gas sensing properties of TiO₂ nanoparticle thin films for biomedical applications are also in progress.

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