Bottom-up synthesis of nanostructured materials by Pulsed Laser Deposition : from clusters to functional films

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INTRODUCTION

Metal and metal oxide films show interesting properties for a number of technological applications such as catalysis, gas sensing, medicine, energy production and storage. For such applications, materials with enhanced performances can be designed through a fine tuning of the morphology and structure down to the nanoscale. In the synthesis of nanostructured materials with tailored physical and chemical properties, the control of the deposition process and its role in determining the properties play a fundamental role. In particular when the synthesis is based on the production and the assembling of nanoparticles/clusters in a bottom-up approach the control and the characterization of the building blocks is of great importance.

Among various deposition techniques Pulsed Laser Deposition (PLD) in a background gas atmosphere has proven to be particularly versatile for the production of nanostructured films and surfaces [1-3]. The expansion dynamics of the ablation plasma plume is strongly modified by the presence of a background gas. In this case spatial confinement and collision rate of ablated species increase with increasing the pressure resulting in cluster nucleation and in a reduced cluster kinetic energy thus affecting the film growth processes [4]. In addition the use of reactive gases such as oxygen permits to deposit oxidized species starting from metallic targets and opens the way for the production of materials with tailored morphology, structure and composition.

EXPERIMENTAL
Films were grown by PLD at room temperature. UV laser pulses in the nanosecond regime (~10 ns) were focused on a metal target (W, purity 99.99%; Ti, purity 99.99%). Energy density in the 1.5-4.5 J/cm² range was chosen to maximize deposition rates while minimizing droplet ejection from the target. The time integrated visible plume length $l_p$ was measured from plasma plume pictures taken through a viewport (orthogonal to the plume axis) by means of a digital camera. The UHV compatible deposition chamber is equipped with a gas inlet system, a mass flow controller and pressure gauges, thus allowing pressure control from $10^{-7}$ Pa to atmospheric pressure. Background gases (He, Ar, O₂ and mixtures) are used with typical pressure in the 10-200 Pa range and target-to-substrate distance $d_{TS}$. The system is connected to a UHV chamber (base pressure $5 \times 10^{-11}$ mbar) hosting surface preparation techniques and a variable temperature STM for in-situ scanning tunneling microscopy and spectroscopy (STM/STS). STM measurements were performed in constant current mode with home made etched W tips. SEM micrographs were acquired with a Zeiss Supra 40 field emission SEM. Micro-Raman measurements were performed with a Renishaw InVia spectrometer (spectral resolution 3 cm⁻¹) using the 514.5 nm wavelength of an Ar⁺ laser.

![SEM images and plasma plume pictures](image)

Figure 1. SEM images (in plane and cross sectional) and pictures of the plasma plume of TiOₓ films deposited at different Ar:O₂ background gas pressures corresponding to $L<1$ left column; $L\approx 1$ middle column and $L>1$ right column.
RESULTS AND DISCUSSION

We here show that by playing with the background gas type and pressure and the target-to-substrate distance a fine tuning of morphology, structure and composition can be reached for a number of metals (e.g. W, Ti, Pd, Ag) and their correspondent oxides. In particular we introduced the non-dimensional parameter $L$, defined as the ratio of the target-to-substrate distance $d_{TS}$ to the time integrated visible plume length $l_p$ ($L = d_{TS}/l_p$) which permits to tune the aggregation/deposition mechanisms [5]. Film morphology can be varied from compact and dense (when $L<1$) to columnar and nanostructured (when $L=1$) up to highly porous foam-like (when $L>1$) as shown in Fig. 1. Correspondingly the mass density for both W/WO$_x$ and TiO$_x$ films shows a variation of more than one order of magnitude as shown in Fig.2.

As deposited film structure can be varied from amorphous to nanocrystalline by changing the background gas pressure as shown by Raman and XRD analysis [6]. In order to independently control morphology and structure, we varied the oxygen content while maintaining a constant pressure by means of different Ar:O$_2$ mixtures (from 1:4 to 4:1). Films with the same morphology possess increasing oxide content with increasing oxygen partial pressure [7]. Moreover different oxide phases can be obtained by post-deposition thermal treatments. In particular amorphous TiO$_x$ films thermally annealed at 400 °C show a different anatase/rutile content which depends on the starting morphology [8].

Figure (2) : Film density of W/WO$_x$ and TiO$_x$ films as a function of background gas pressure during deposition.
In order to characterize the first stages of film growth and the size and deposition kinetic energy of building blocks, pulsed laser deposits on atomically flat surfaces (e.g. Si(111), HOPG, Au(111)) have been investigated in ultra high vacuum (UHV) by in situ STM [9]. STM is employed to study isolated W and Pd clusters revealing that the deposition kinetic energy is strongly affected by the target-to-substrate distance while the cluster size distribution mainly depends on the gas pressure. Fig. 3 reports the case of W deposition. A few laser shots (3-5) at 10 Pa Ar \((L<1)\) on Au(111) corresponds to high kinetic energy deposition and resulting deposits are characterized by fragmentation of ablated species and damage formation of the substrates surface. On the contrary deposition at 40 Pa Ar \((L>1)\) permits to obtain isolated clusters. Energy deposition regimes can be thus tuned to obtain cluster-assembled films composed by nano-sized building blocks (1-10 nm typical size) as evidenced in STM images at increasing coverage. Therefore PLD allows us to design new materials with tailored properties by selecting size, composition and deposition kinetic energy of the building nano-units constituting the material [10].

![Figure 3: Constant current in situ STM images of W deposits at different deposition conditions. A) 10 Pa Ar, L<1 and B) 40 Pa Ar, L>1](image)

Functional properties are tested revealing enhanced performances for specific applications. In particular gas sensing properties of WO₃ nanorods formed after thermal treatment of disordered WOₓ; catalytic properties of Pd clusters deposited on Al₂O₃ support and self cleaning properties of hierarchical cluster-assembled TiO₂ films [9]. Such approach reveals the potential impact of a complete characterization of the PLD bottom-up process from the single building unit to the assembly of a nanostructured film and finally to application.

**REFERENCES**