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Structural characterization of nanoparticles-assembled titanium dioxide films produced by ultrafast laser ablation and deposition in background oxygen

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ABSTRACT

Ultrafast laser ablation of titanium dioxide and deposition of nanoparticles-assembled films in oxygen ambient gas at pressures going from high-vacuum up to several mbar is investigated. We identify various regimes of the plumes propagation into the background gas as well as of the material deposition rate. These reflect on the structural characteristics of the nanoparticles-assembled films: the film morphology changes from a structure with glue-like nanoparticulates, at low pressure, to a highly porous assembly of individual nanoparticles, at larger pressure. Our findings indicate that background gas pressure provides an interesting key for additional control on the structural characteristics of oxide nanostructures produced by femtosecond laser deposition.

1. Introduction

Ultrafast laser ablation (ULA) is the explosive removal of material excited to high temperature and pressure through irradiation with intense laser pulses of femtosecond (fs) duration. ULA in high vacuum has been rather extensively investigated, evidencing that it leads to the direct generation of nanoparticles (NPs) of the target material [1–4]. Deposition of the ULA material on a suitable substrate offers a practical route for the synthesis of NPs and NPs-assembled films of different materials by pulsed laser deposition (PLD) [3–7]. PLD with femtosecond pulses (fs-PLD) has been applied for the growth of oxide thin films [8,9], as well as of oxide nanostructures in the form of nanoparticles, nanorods and nanowires assembly [10–12]. For example, catalyst-free growth of oxides nanorods was achieved by fs-PLD in a low pressure background gas (N_2 and O_2 mixture at $\approx 10^{-2}$ mbar) [11]. Moreover, oxide nanowires were obtained at atmospheric pressure by fs-PLD assisted by Au NPs acting as catalyst on the substrate surface [12].

The use of an ambient gas is a well-established method employed in the PLD technique to control highly energetic species since the gas acts as a moderator of the ablation plume during the flight from the target to the substrate [13,14]. The study of the interaction of ablation plumes with a background gas has been considered rather extensively for nanosecond pulses [13–17], while studies aiming to ascertain meaningful correlations among the different ULA parameters, the structural and functional properties of the deposited films, and the plume dynamics in a background gas are still scarce [18–20].

In this letter, we examine the effects of the ambient gas pressure (from high-vacuum up to ≈10 mbar) during fs-PLD of titanium dioxides (TiO_2), a wide bandgap (3.0–3.2 eV) semiconductor which in nanostructured form is considered as a very relevant material for a number of emerging applications, crossing traditional disciplinary boundaries in energy and environmental technologies [21–24]. TiO_2 has excellent optical and electronic properties for a widespread use (e.g., in photocatalytic air purification and environmental sanitation, self-cleaning coatings and electrodes for photovoltaic solar energy conversion, gas sensing, etc.). As for other functional oxides, e.g., tin oxide and zinc oxide [25–27], the nanostructure characteristics critically influence the performances of TiO_2-based devices, particularly those based on photocatalysis, and

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reactivity to changes in the external environment [28]. Developing well-controlled routes for the synthesis of high-quality TiO_2 nanostructures can thus be of relevance to many applications.

Several studies have been carried out on the fabrication of TiO_2 nanostructured films by PLD with nanosecond laser pulses (see, e.g., Refs. [29]–[31], and papers therein quoted). These studied evidence the production of TiO_2 nanostructured, crystalline deposits whose properties depend on the deposition conditions, namely background gas (vacuum, Ar and O_2) pressure and laser pulse wavelength. In some cases a pure Ti target is ablated and titanium dioxide is formed either in the interaction with oxygen background gas or on the substrate [32]. Optical emission spectroscopy analysis of the TiO_2 ablation plume showed the presence of Ti and O neutrals and Ti ions, while no sizeable signature of emission from excited molecules or nanoclusters was observed in the registered spectra. Nevertheless, microscopic particles were present on the surface deposits, which reduce at shorter wavelength (e.g., 266 nm). On the contrary, the few previous studies on fs-PLD of TiO_2, carried out in high vacuum or at low oxygen background pressure ($\approx 10^{-2}$ mbar), have shown that nearly stoichiometric TiO_2 NPs with average diameters of ≈20–50 nm are produced [10,32]. Moreover, ablation plume analyses in high vacuum conditions show the presence of a significant component of NPs in the ablated material, and the nanostructured deposit mainly results from the collection of these NPs on the substrate [10,32].

Here we investigate the influence of the background oxygen pressure on the properties of TiO_2 NPs-assembled films, from high vacuum up to several mbar. Our experimental findings demonstrate an interesting influence of the background gas pressure: the film morphology changes from a cauliflower-like structure with NPs embedded in glue-like nanoagglomerates, at low pressure, to a highly porous assembly of individual NPs, at larger pressure. This observation is correlated with the NPs plume dynamics and deposition rate dependence on the background gas pressure. These outcomes are particularly relevant to tune oxide NPs films characteristics for applications where the nanoscale porosity, and the high-surface brought about by the NPs can be beneficial to facilitate reactions with the interacting medium as, e.g., in photocatalytic and sensing applications.

2. Experimental methods

Fs laser pulses (527 nm, ≈300 fs full width at half maximum) were used to produce ablation of a commercial TiO_2 rutile target (SurfaceNet). The laser beam was focused at ≈45° onto the target surface with a 25 cm focal length lens. By measurement of the laser impact region as a function of the laser pulse energy [33,34], a spot area on the target of $(4.4 \pm 0.4) \times 10^{-4}$ cm^2 was estimated. Ablation was induced by laser pulses at a fluence of 1.4 J/cm^2, corresponding to about 10× the TiO_2 damage threshold for 527 nm, ≈300 fs laser pulses [35]. The target was mounted on a rotating holder to avoid local drilling.

NPs-assembled films were deposited by collecting the produced NPs on Si(1 0 0) substrates, held at room temperature and located 4.0 cm a part from the target surface. The morphology of the TiO_2 NPs-assembled films was analyzed by a Zeiss ΣIGMA field emission scanning electron microscope (FESEM) with a nominal resolution of 1.3 nm at 20 kV, while their crystallographic structure was investigated by means of X-ray diffraction (XRD), using a Rigaku D/Max-B powder diffractometer with Cu Kα radiation, in the $\theta/2\theta$ configuration. The diagnostic tools for the analysis of the fs-PLD process included a fast intensified-charge-coupled device (ICCD) for time- and space-resolved imaging of the ULA plumes, and a quartz crystal microbalance (QCM). The deposition rate measurements were carried out by placing the QCM at the substrate location.

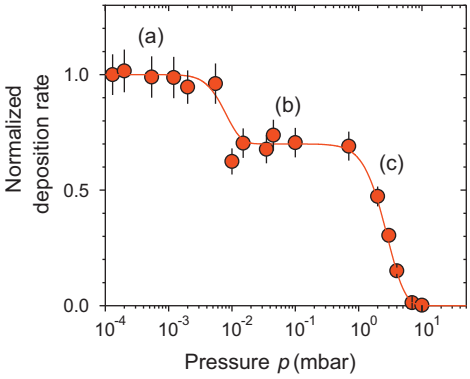

Fig. 1. Variation of the deposition rate as a function of the background oxygen pressure, p. The deposition rate is normalized to the value registered in high vacuum. The solid curve is a guide to the eye. The letters identify the three different regimes characterizing the pressure dependence of the deposition rate.

Typically, ≈3300 laser pulses at 33 Hz were used for deposition rate measurements, due to the QCM limited sensitivity. Plume images were acquired by reducing the rep. rate at ≈1 Hz with a mechanical shutter and accumulating 10 laser ablation events.

3. Results and discussion

Fig. 1 reports the relative variation of the deposition rate as a function of the background gas pressure, p. In Fig. 1, the deposition rate is normalized to the value (12 ± 1 ng/s) registered in high vacuum (HV). We can clearly identify the existence of three different deposition regimes. At low pressure, a constant deposition rate is observed for $p < 2 \times 10^{-3}$ mbar [regime (a)]. At intermediate pressure ($10^{-2} < p < 10^{-1}$;mbar), this is followed by a plateau region characterized by a ≈30% reduction of the deposition rate with respect to HV [regime (b)]. Then, for $p > 1$ mbar, a third region, characterized by a progressive decrease of the deposition rate [regime (c)], is observed. This behavior can be related to the effects of the background gas pressure on ULA plume species [18]. In fact, the ablated material produced during ULA of TiO_2 consists of two main components [35], similarly to what is generally observed in ULA of metals and elemental semiconductors [1,2,4]. An atomic/molecular plume, composed of Ti and TiO species, and flowing at high velocity (≈10^4 m/s), is followed by a slower population of aggregates (clusters and NPs), which expands at a much smaller velocity (≈5×10^2 m/s) [35]. The oxygen background gas, acting differently on the atomic and NPs plumes [18], gives rise to the presence of the different regimes observed in Fig. 1.

Fig. 2(a) reports characteristic images of the TiO_2 atomic plume at two pressures representative of the regimes (a) and (b) of Fig. 1. In the left panels of Fig. 2(a) we observe that in HV the fast atomic plume is characterized by a very forward-peaked expansion into vacuum, reaching distances of few tens of mm from the target surface on a timescale of few hundred nanoseconds. At a delay of 2.5 μs, the atomic plume has significantly reduced its emission intensity and already moved to distances larger than ≈30 mm, and only the NPs plume, whose expansion only occurs after a much longer delay, is visible close to the target surface.

In the regime (b), the background gas pressure strongly affects the atomic plume expansion, as evidenced in the right panels of Fig. 2(a) corresponding to $p = 5 \times 10^{-2}$ mbar. From the images we can appreciate that in this regime the atomic plume expansion is effectively confined as its front follows an almost stationary behavior, while its shape becomes more spherical at longer delay. This indicates that the transition between regimes (a) and (b) is strictly related to the progressive confinement of the atomic plume, which is eventually halted over distances shorter than the