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In situ STM of pulsed laser nanostructured deposits: First stages of film formation

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Abstract

In the synthesis of nanostructured thin films the characterization of the growth processes plays a fundamental role for the control of the film and surface properties. Moreover when the deposition technique is based on the production and the assembling of nanoparticles/clusters the characterization of the precursor size distribution is of fundamental importance.

We have designed a pulsed laser deposition (PLD) apparatus for the production of nanostructured thin films and surfaces, connected to a UHV variable temperature scanning tunneling microscope (STM). The whole system is devoted to the synthesis and in situ study of nanostructured and nanoporous functional metal and metal oxide films and surfaces. We have deposited W nanoparticles produced by a few hundreds laser pulses in order to investigate the initial mechanisms of the film growth. Different deposition conditions have been explored by controlling the laser generated plasma expansion through a background gas in the PLD chamber. STM measurements have been performed on W thin films deposited on different substrates to study both the size distribution and the aggregation of the precursors on the surface. Although substrate effects must be taken into account, the control of the background gas pressure and of the target-to-substrate distance allows to produce surfaces with different morphologies. This opens the possibility to tailor the material properties through the control of the size and deposition energy of the building nano-units.
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1. Introduction

In recent years great efforts have been devoted to the controlled synthesis of nanostructured materials. Since the nanostructure plays a fundamental role in determining material properties (electronic, optical, magnetic, mechanical, etc.), it is in principle possible to engineer new functional systems by carefully tailoring their structure at the atomic and nanometer scale. One of the routes adopted to synthesize nanostructured thin films is the controlled assembling of clusters [1–3]. Among different chemical and physical assembling techniques, pulsed laser deposition (PLD) is particularly interesting due to its versatility in the deposition of materials, even with a complex stoichiometry [4]. PLD in vacuum permits to produce films assembled atom by atom, achieving even epitaxial growth in particular conditions (i.e. heated subtrates).

Conversely, in the presence of a suitable background gas pressure, laser ablation may result in cluster formation during the plume expansion (see e.g. [5]). In the synthesis of nanostructured thin films the characterization of the growth processes plays a fundamental role for the control of the film and surface properties. In particular, when the deposition technique is based on the production and assembling of nanoparticles/clusters, the characterization of the precursor size distribution as well as of the first stages of film formation is of fundamental importance. Among other techniques, scanning tunnelling microscopy (STM) has been widely employed to image clusters and nanoparticles on different surfaces (see e.g. [6–8]).

Tungsten oxide is particularly interesting due to its electrochromic [9], catalytic and gas sensing properties [10], and the control of the specific surface area (i.e. the porosity) and of the grain size can be exploited to increase conduction sensitivity when a target gas molecule is adsorbed on the surface [11]. We have already reported on the pulsed laser deposition of tungsten and tungsten oxide nanostructured films,

with different degrees of nanoporosity, by controlling the gas type (inert and reactive) and its pressure in the deposition chamber [12].

This work focuses on the deposition and in situ STM imaging of the first stages of PLD film formation, addressing the role of plume expansion in a background gas (namely Ar). In situ characterization is fundamental to ensure the observation of film morphology in its growth conditions, for spontaneous oxidation is observed in PLD tungsten films deposited in inert gases when exposed to ambient atmosphere [12].

2. Experimental details

We have designed and built a PLD apparatus for the deposition and in situ characterization of supported clusters, nanoparticles and thin films. In particular, both STM and atomic force microscopy (AFM) measurements can be performed on clusters and cluster aggregates deposited on atomically flat surfaces, in order to follow the first stages of growth of different cluster-assembled materials. The PLD apparatus exploits the nanosecond (10–15 ns pulse duration) UV (248 nm wavelength) pulses of a KrF excimer laser. The UHV compatible PLD chamber is evacuated by a 500 l/s turbo pump and a dry roughing pump. A mass flow controller permits to introduce different gases at a controlled pressure. The PLD chamber is connected to a UHV (5×10^{-9} Pa) analysis chamber hosting an e-beam evaporator equipped with a tungsten rod as the evaporant material, an ion gun for surface preparation and a STM/AFM variable temperature Omicron UHV VT-SPM.

We have deposited on atomically flat surfaces, namely Highly Oriented Pyrolytic Graphite (HOPG, see e.g. [13,14]) and Si(1 1 1)7 × 7 [15] at room temperature, a small amount of material produced by ablation of a W target with a small number of laser pulses (300). The substrate surfaces were prepared and degassed in the UHV analysis chamber, then transferred via a mag-probe UHV transfer system in the deposition chamber (usually kept at a pressure of 5×10^{-6} Pa), where they were exposed to a background Ar pressure (in the range 10–100 Pa) for the duration of the laser deposition process (300 laser pulses corresponding to 30 s at 10 Hz). Laser pulses (energy density about 4.5 J/cm^2) are directed onto a W target (99.99% purity). The target-to-substrate distance ($d_{TS} = 50$ mm) was kept constant during deposition. The deposition rate was about 0.1–0.2 nm/s (it varies with the background gas pressure), as measured by a quartz micro-balance, i.e. we deposited a few nanometers estimated equivalent thickness and this resulted in an almost complete coverage of the substrate surface. The samples were finally re-transferred in the STM analysis chamber where room temperature STM measurements were performed in constant current mode with home-made W tips. Prior to deposition we checked by STM that atomic resolution was achievable for HOPG even after exposure to the deposition atmosphere, while atomic steps were detected, but 7 × 7 reconstruction was lost, for Si(1 1 1) substrates. Typical STM tunnelling currents (~nA) resulted in a drift of the observed deposited W

aggregates, probably due to sticking of the deposits on the STM tip. Better images were obtained by keeping the tip far from the surface, i.e. with a very low tunneling current (a few pA) and a relatively high tunneling potential (3–8 V).

3. Results and discussion

STM images (100 nm × 100 nm) of deposits on Si(1 1 1) as a function of Ar background deposition pressure, from 10 to 100 Pa, are shown in Fig. 1 (left column). The mean aggregate size increases from a few nm to more than 10 nm when increasing the background gas pressure from 10 to 100 Pa. In particular higher resolution STM images (20 nm × 20 nm) shown in Fig. 2 and the grain size distribution reported in Fig. 3 (computed from the 100 nm × 100 nm images) clearly reveal that at 10 Pa the surface is formed by assembling of aggregates whose diameter is about 1–3 nm (2.2 nm mean value) while moving to 40 Pa the building units are in the 2–6 nm diameter range (3.5 nm mean value). The grains observed in the 100 Pa deposit have a wide size distribution and the bigger ones appear to be constituted themselves by an assembly of finer nano-units. It has also to be noticed that when the deposition pressure is increased, the size distribution looks more dispersed (see Fig. 3) and this results in the growth of a more open and rough structure of the deposited surface (see Fig. 1). These observations are in agreement with SEM images (not shown, see [12,16]) of films (several thousands laser shots, film thickness about 100 nm) grown on Si substrates in the same conditions. They show a compact and smooth surface at a deposition pressure of 10 Pa or less; the surface roughness increases at higher pressures, until a sponge-like, porous structure, characterized by a very high specific surface area, is obtained for Ar pressures higher than 100 Pa [12,16].

Two different substrates (i.e. Si(1 1 1) and HOPG) have been exploited to investigate the effect of the substrate on the first stages of film formation. This allows to distinguish clusters or aggregates grown after deposition due to mobility and aggregation of the impinging species on the substrate, from clusters formed in the plasma plume and then deposited and assembled on the substrate. A different morphology is observed at the same Ar pressure for deposits on HOPG and Si even though, a similar morphology trend is observed as a function of the gas pressure on both Si and HOPG substrates, as clearly shown in Fig. 1.

In particular on HOPG the film nanostructure is composed by slightly larger building units than on Si at the same Ar pressure. This could be ascribed to coalescence effects due to a higher cluster mobility (and a different interface energy) on HOPG with respect to Si(1 1 1) observed during STM measurements [17]. In fact on HOPG standard tunneling conditions (a few nA, a few V), corresponding to a smaller tip-to-surface distance, resulted in a 'cleaning' effect capable to totally remove the W deposit from the HOPG surface. Furthermore, W atom-by-atom cluster formation on HOPG due to mobility and surface and interface energy effects is observed for W deposits (complete coverage) obtained by UHV e-beam evaporation. The STM image of such a surface (see