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Nanoporous cluster-assembled WO_x films prepared by radio-frequency assisted laser ablation

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ABSTRACT

The influence of substrate temperature and ambient gas pressure-composition on the characteristics of WO_x films synthesized by radio-frequency assisted pulsed laser deposition (RF-PLD) are studied with the aim to obtain nanostructured films with large surface area that appear promising for gas sensing applications. A tungsten target was ablated both in chemically reactive molecular oxygen at 5 Pa and in a mixed oxygen–helium atmosphere at 700 Pa. Corning glass was used as the substrate, at 473, 673 and 873 K. Other deposition parameters such as laser fluence (4.5 J/cm^2), laser wavelength (355 nm), radio-frequency power (150 W), and target to substrate distance (4 cm) were kept fixed. The sensitivity on the deposition parameters of roughness, morphology, nanostructure and bond coordination of the deposited films were analysed by atomic force microscopy, scanning electron microscopy, transmission electron microscopy and micro-Raman spectroscopy. The role of the investigated process parameters to nanoparticle formation and to the development of an extended nanostructure is discussed.

1. Introduction

The wide-gap semiconductor tungsten trioxide (WO_3) is an important electro-chromic material mostly used for gas and humidity sensors, low voltage varistors [1,2], and smart and optical windows [3]. Applications of WO_3 in catalysis, including selective oxidation of organic compounds are explored [4]. In the above cases high values of specific surface area A_s, as obtained in cluster-assembled (CA) films are advisable. Pulsed laser deposition (PLD) in an ambient gas allows depositing CA materials with different morphologies and A_s values, besides different degrees of crystallinity, mechanical stability and adhesion to the substrate. Clusters, formed mainly by collisions in the propagating ablation plasma plume [5], land on the substrate where they migrate and aggregate with each other. Depending on the balance between the average kinetic energy per particle at landing and the cluster/nanoparticle (NP) cohesion energy, the growing film keeps a memory of the incoming building blocks, or not. This affects film nanostructure and morphology. The dependence of WO_x film properties on deposition parameters was investigated for evaporated [3] and sputtered [6] films. The composition, structure and morphology of WO_x films deposited ablating with an excimer laser a sintered WO_3 target in molecular oxygen atmosphere, at a pressure not exceeding 20 Pa sensitively depends on substrate temperature [7]. We adopted [8–10] a hybrid deposition technique, combining the advantages of PLD in an ambient gas (O_2) with the enhanced reactivity associated to a beam of excited and ionised atoms and molecules produced by a radio-frequency (RF) discharge through oxygen. This allows overcoming the detrimental formation of oxygen vacancies in the film and at the film–substrate interface. After a thorough exploration of the role of laser fluence, RF power and gas pressure on film roughness, nanostructuring and crystallisation [8,9] here we analyse substrate temperature and gas composition at high pressure, focussing on *selected* samples. Direct nanostructure imaging by transmission electron microscopy is correlated to Raman spectroscopy data. Scanning and atomic force microscopies provide trends of morphology evolution as a function of process parameters in WO_x films. Our aim is to find suitable conditions to synthesize WO_x films largely made of nanoparticles (NPs) that can be candidates for miniaturised gas sensors.

2. Experimental

A Tungsten target was ablated in pure O_2 at 5 Pa and in a gas mixture consisting of O_2 and He in the same relative proportion at 700 Pa. The set-up was described elsewhere [8]: the laser wavelength at 355 nm, the laser fluence was fixed at 4.5 J/cm^2 and the RF power at 100–150 W. Corning glass substrates, at temperatures T_s of 473 K, 673 K, and 873 K, were placed in front of the target, parallel to it, at a distance of 4 cm. The average film thickness, as estimated by the ablation rate, ranged between 80 and 110 nm. In Table 1 the

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Table 1
Experimental parameter values adopted to deposit WO_x thin films.

Sample	p_{gas} (Pa)	T_s (K)	N_{pulses}	P_{RF} (W)
83	5 O_2	473	15.000	100
91	5 O_2	673	12.000	150
92	5 O_2	873	12.000	150
438	350 O_2 + 350 He	673	12.000	150
440	350 O_2 + 350 He	873	12.000	150

deposition parameters adopted for each sample are summarised. The parameters in bold are those specifically addressed in this study.

The details of the surface morphology of the samples was complementarily studied by atomic force microscopy (AFM), using a Nomad type instrument, in the intermittent contact mode [8], analysing (10 × 10) μm^2 areas and by scanning electron microscopy (SEM), using a Zeiss Supra 40 field ion microscope without sample metallization. Film nanostructure and the formation of WO_x nanoparticles were investigated by transmission electron microscopy (TEM) with a Zeiss Leo 912AB microscope working at 80 kV. Pictures were acquired with a charged coupled device (CCD) Esi Vision ProScan camera, with a resolution of 1024 × 1024 pixels. TEM observations were performed on material gently scraped from the deposited films onto Formvar covered TEM grids. The local bonding coordination of the films was studied by micro-Raman spectroscopy, in backscattering configuration, using the 514 nm line of an Ar^+ laser whose power was fixed at 0.5 mW to avoid film local annealing and photo-induced structural modifications [8].

3. Results and discussion

Figs. 1 and 2 display representative SEM micrographs and the corresponding AFM scanned surfaces of samples deposited in O_2 at 5 Pa, at substrate temperature T_s of 673 K and 873 K. Film morphologies change from wavy, structureless (Fig. 1a, sample 91), with occasional particles with size around 100 nm, to porous (Fig. 2a, sample 92), with a few big irregularities and many scattered NPs, sized about 50 nm. The surface morphology of the film deposited at the lowest T_s = 473 K (sample 83) is smooth, again featureless, similar to sample 91. AFM confirms strong morphology changes associated with T_s increases, though film roughness remains almost unchanged: the few big, isolated NPs (sample 83, not shown) become smaller, more crowded on the surface (Fig. 1b), until eventually film

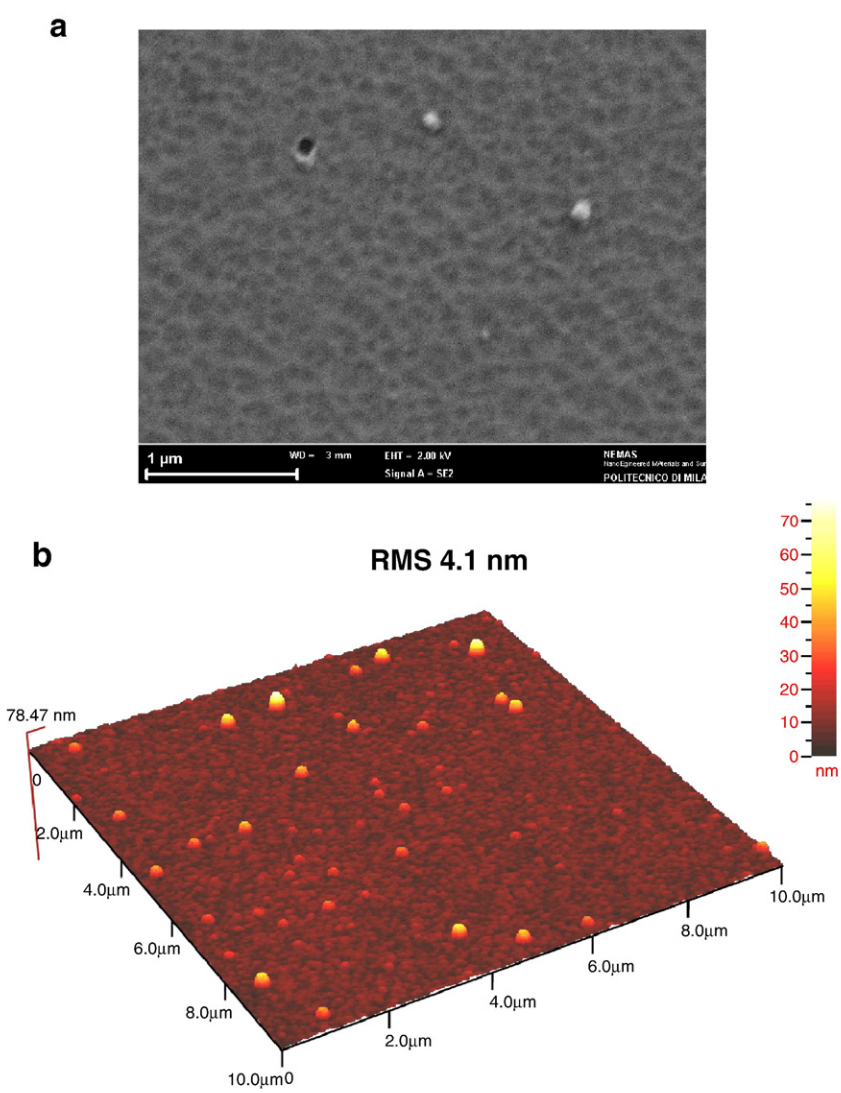

Fig. 1. Representative surface microstructure (a) of a film (sample 91) deposited at p_{O2} = 5 Pa and T_s = 673 K. AFM image (b) of the same sample.