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Synthesis and characterization of tungsten and tungsten oxide nanostructured films

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Abstract

Nanostructured tungsten and tungsten oxide films have been synthesized by pulsed laser deposition (PLD) in different atmospheres (He, Ar, dry air). The control of the gas pressure in the deposition chamber allows to vary the morphology of the deposited films (studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM)) ranging from a compact ultrasmooth structure to a porous nano and mesostructure characterized by a high fraction of voids and by a large specific area. The presence, the structure and the degree of crystallinity of tungsten oxide have been investigated by Raman spectroscopy. By varying the pressure of the background inert gas (He, Ar) in the 1–1000 Pa range we obtain metallic films with different degrees of spontaneous oxidation when exposed to the atmosphere. Deposition in dry air permits to grow nanostructured tungsten oxide films characterized by different degrees of crystallinity, ranging from amorphous to nanocrystalline.

Keywords: Pulsed laser deposition; Tungsten; Tungsten oxide; Nanostructured thin films

1. Introduction

Tungsten and tungsten oxide films are interesting materials for novel technological applications. Properties of tungsten and tungsten oxide thin films have been explored for electrical contacts in microelectronics [1,2] and for the development of sensors and functional coatings (e.g. smart windows) [3–6]. Increasing interest is devoted to tungsten and tungsten oxide for catalytic applications such as methanol oxidation for fuel cells [7,8], selective oxidation of organic compounds [9], hydrodesulfurization of fuels [10] and isomerization reactions [11,12]. The capability to synthesize bulk materials, films and surfaces with controlled nano and mesostructure opens up the way to tailor the physical (e.g. effective surface area, energy gap) and chemical (e.g. surface reactivity, stoichiometry) properties in view of device development. In this context, the increase of the specific effective surface and the comprehension and control of the electric and optical properties of tungsten oxide coatings is of great importance for the development of the mentioned applications.

Pulsed laser deposition (PLD) is a versatile technique for the synthesis of a wide range of materials [13,14]. The control of the ablation plasma expansion permits to vary the dynamics of the ablated species (atoms, ions and clusters) during their flight before deposition on the substrate. Plume expansion is affected by a background gas in the deposition chamber [15,16]. Provided the pressure is high enough, a background gas increases the collision rate thus favoring cluster formation in the plume [17]. Moreover, clusters loose energy in collisions impinging onto the substrate with a reduced kinetic energy after diffusing in the background atmosphere [18]. PLD in air and N_2 at atmospheric pressure has been already exploited to produce tungsten nanoparticles [19]; some works have been recently devoted to the PLD deposition of tungsten oxide nanostructured films [20,21]. In these cases deposition parameters have been explored and experiments were mainly focused on the optimization of a specific property (i.e. gas sensing and electrochromism).

We report on the capability to grow tungsten and tungsten oxide films with different and controlled nano and mesostructure, ranging from compact to highly porous, by varying the

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pressure of a background gas in the 1–1000 Pa range. Pressure and gas type (inert or reactive) influence also the oxidation pathway and the structure of tungsten oxide films.

2. Experimental details

W and WO_3 films have been grown by PLD on silicon substrates at room temperature. UV laser pulses in the nanosecond regime (10–15 ns), from a KrF excimer laser (248 nm wavelength), were focused on a W target (purity 99.99%) with an energy density of roughly 4.5 J/cm^2. This value was chosen in order to maximize deposition rate while minimizing droplet ejection from the target. Films were grown performing 4500 laser pulses at 10 Hz repetition rate (deposition time 7.5 min), with target-to-substrate distance fixed at 50 mm. The deposition rates vary in the 0.2–2 Å/s range moving from deposition in vacuum to 100 Pa He. The UHV compatible deposition chamber is equipped with a 500 l/s turbomolecular pump backed up by a scroll dry pump. The system is equipped with a gas inlet system, a mass flow controller and a full range pressure gauge, thus allowing pressure control over the 10^{-7} Pa to atmospheric range.

SEM micrographs were acquired with a Cambridge Stereoscan using 30 keV primary acceleration voltage and 10 pA probe current. High-resolution images were acquired with a cold field emission Hitachi S-4800 scanning electron microscope. Atomic force microscopy (AFM) measurements were performed with a Thermomicroscope CP Research in non-contact mode with high resonance frequency silicon cantilevers. The film surface root mean square (rms) roughness was estimated from the surface height $z(x, y)$ data measured by AFM. Micro-Raman measurements were performed with a Renishaw InVia spectrometer using the 514.5 nm wavelength of an Ar^+ laser. Spectra were acquired by a 1800 greeds/mm grating, a super-notch filter (cut-off at 100 cm^{-1}) and a Peltier-cooled CCD camera, allowing a spectral resolution of about 3 cm^{-1}.

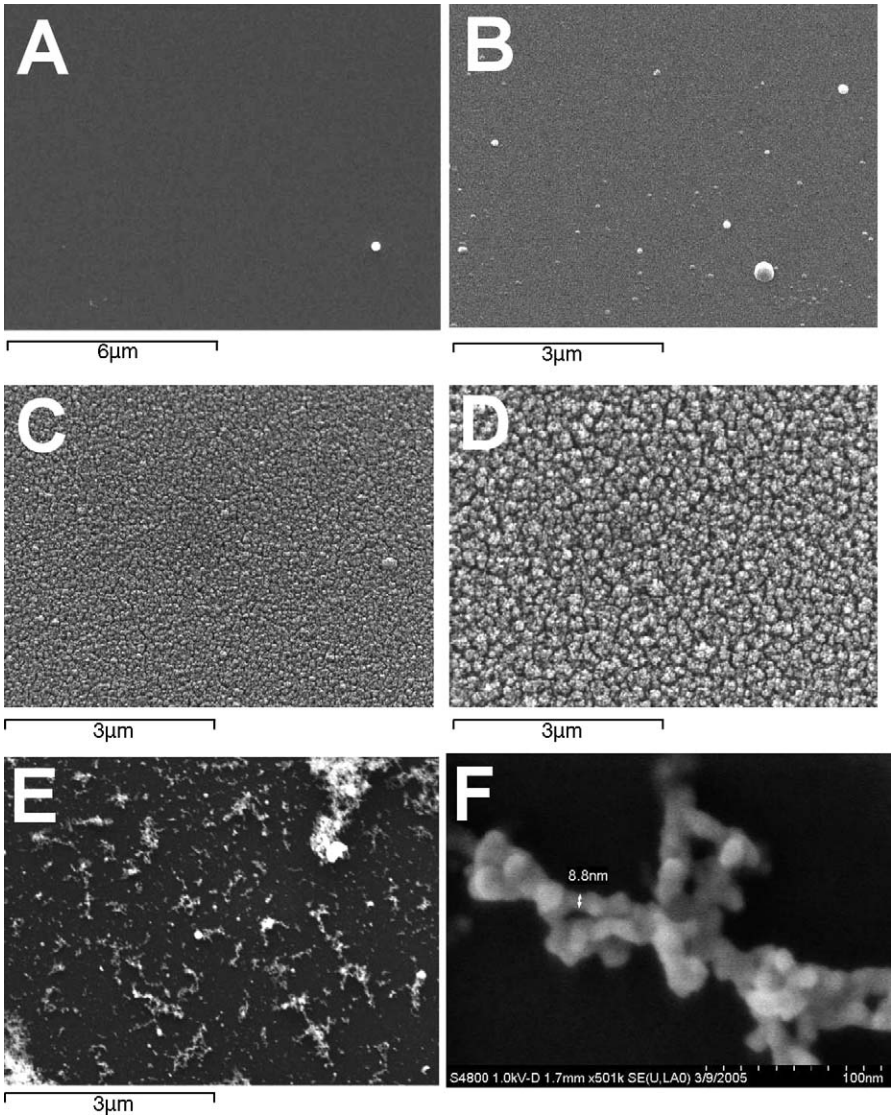

Fig. 1. SEM micrographs of tungsten films deposited in Ar at (A) 1 Pa, (B) 20 Pa, (C) 40 Pa, (D) 60 Pa, (E) 400 Pa, and (F) high resolution SEM image of a snowflake structure deposited at 1000 Pa dry air.