Pulsed Laser-Induced Effects in the Material Properties of Tungsten Thin Films

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Abstract. In this work we present evidence of photo-induced effects on crystalline Tungsten (W) films. A frequency doubled Nd:YAG (5ns) laser was used in our experiments. The W thin films were deposited on silicon substrates by the DC-sputtering technique using W (Lesker, 99.95% purity) targets in an argon atmosphere. The crystalline phase of the deposited W films was determined by X-ray diffraction. Our experimental results show clear evidence that several events take place as a consequence of exposure of the W films to the laser nanosecond pulses. One of those events has a chemical effect that results in a significant degree of oxidation of the film; a second event affects the structural nature of the initial W material, resulting into a material phase change; and a third event changes the initially homogeneous morphology of the film into an unexpected porous material film. As it has been confirmed by the experiments, all of these effects are laser fluence dependent. A full post exposure analysis of the W thin films included Energy Dispersive Spectrometry to determine the degree of oxidation of the W film; a micro-Raman system was used to explore and to study the transition of the crystalline W to the amorphous-crystalline WO₃ phase; further analysis with Scanning Electron Microscopy showed a definite laser-induced porosity which changes the initial homogeneous film into a highly porous film with small features in the range from 100 to 300 nm.

1. Introduction

Laser-induced local oxidation in metal films and plates has been reported previously for some metals as: titanium [1], chromium [2] and stainless steel [3]. J. L. Jiménez-Pérez et al. [1] have reported results about laser oxidation in titanium films. They found using Raman microscopy that the pulsed-laser irradiated material was composed by the TiO₂ rutile phase. In other work, J. Lian et al. [2] have used a Nd-YAG laser to irradiate chromium films with the fundamental line (1064 nm). In that case, the authors identified by X-ray diffraction technique the presence of the Cr₂O₃ crystalline phase in the irradiated material. In this paper, we present the local effects induced in W-W₃O film by nanosecond pulses of Nd-YAG laser.
2. Experimental
2.1 Growth of the films
Tungsten (W) films were grown by the dc-magnetron sputtering technique using an Argon gas atmosphere. A target of 3 inch of diameter was used (Lesker, 99.95% purity). The deposition parameters were: a DC-Sputtering power of 150 W, the substrate to target distance was fixed at 40 mm, the deposition time was 20 minutes and the substrate temperature was kept at 150°C. The pre-cleaned silicon and glass substrates were placed in a vacuum chamber which was evacuated to a base pressure of about $1 \times 10^{-6}$ mbar using a primary mechanical pump and a secondary turbomolecular pump. The working pressure was $1 \times 10^{-3}$ mbar. A shutter placed between the magnetron and the substrate holder made it possible to clean the target surface before deposition.

2.2 Laser processing experimental set-up
Figure 1 shows the experimental set-up that we utilized to carry out the film laser irradiation. The laser source is a Continuum (Minilite II) frequency doubled Nd:YAG laser, with pulses of ~5ns (FWHM) duration and a 10 Hz repetition rate. The laser beam is transported down to the target film using a vertical configuration micromachining station as it is shown in the schematic of the experimental set-up. We used a 50 cm focal length lens to focus the beam on target. The laser beam had a diameter of 8 mm (FWHM) at the lens location. The 220 μm laser beam waist of the focused beam was experimentally determined using a CCD array in combination with a graticule grid at the beam waist position.

2.3 Films laser exposure processing
Laser exposure of the films was carried out following a computer controlled pattern of laser irradiated segments on the film surface (see figure 2a). The scan speed was kept fixed at 4 μm/sec during exposure, while the fluence per pulse delivered to the film was fixed at 161 mJ/cm². Given the scan speed of 4 μm/sec, the beam waist of 220 μm and the laser repetition rate at 10 Hz, a total number of 550 pulses were delivered at any given spot on the irradiated zone.

2.4 Characterization techniques
The as-deposited films were characterized by X-Ray Diffraction (XRD) using a diffractometer (Siemens, D-5000), Scanning Electron Microscopy (SEM) with a Phillips XL-30 microscope and Energy Dispersive Spectrometry (EDS). The pulsed-laser irradiated zones were analyzed by Raman Microscopy (RM) using the micro-Raman system (HR-800 LabRam), SEM and EDS.

Figure 1. Experimental set-up utilized to carry out the film laser irradiation
3. Results and discussion

The O/W ratio for the as-deposited film obtained from EDS measurement was 0.33. The diffractogram (not showed here) of the as-deposited tungsten film indicated that the film material is a mixture of α-W and β-W (low oxidized tungsten, W₃O) crystalline phases. L. Maillé et al. [4] have reported a morphological and structural analysis of that phases obtained by sputtering.

Figure 2 shows SEM micrographs that correspond to a W-W₃O film. In figure 2(a) we can observe a square pattern recorded with a net fluence of 89 J/cm². Three amplifications of a linear segment of the irradiated zone are showed in Figures 2(b-c). It can be clearly seen that the irradiated surface is constituted by porous material. The porous size is in the range from 100 to 300 nm. The O/W ratio for the irradiated zone was 0.48. Then there is a modest increment of the oxygen content in the irradiated zone.

Figure 3 shows Raman spectra in the interval 600-1200 cm⁻¹ for the following cases: (a) the as-deposited film, (b) Irradiated zone at 89 J/cm² (net fluence) and (c) crystalline monoclinic-WO₃ (Aldrich, 99.99 % purity powder). Raman spectrum 3(c) is composed by two peaks located at 715 and 806 cm⁻¹. These peaks correspond to W-O stretching vibration modes of a ReO₃ type structure. In contrast, Raman spectrum of the as-deposited film don’t present any Raman fine peaks, this is probably due to the metallic feature of the W-W₃O films. Figure 3(b) shows the Raman spectrum corresponding to the pulsed laser irradiated zone at a net fluence of 89 J/cm² (per pulse of 161 mJ/cm²). It can be observed that this spectrum is constituted by three bands centered at 695, 820 and 950 cm⁻¹. The bands at 820 and 695 cm⁻¹ can be associated to the vibration modes of the monoclinic phase of WO₃ (806 and 715 cm⁻¹) [5]. The shift of the bands can be due to the distorted octahedra in the highly sub-stoiquiometric tungsten oxide structure. According to the literature [6], the band at 950 cm⁻¹ is associated to W=O stretching modes of terminal oxygen atoms. This laser-induced porous structure in the films is probably allowing for the formation of the oxygen terminal bonds associated to the 950 cm⁻¹ band in the Raman spectrum as is showed in Fig. 3(b).

Figure 2. Porosity induced on the irradiated surface of a W-W₃O film. a) Square pattern formed by linear segments irradiated at a net fluence of 89 J/cm²; (b), (c) and (d) amplifications of a linear segment showed in (a)
Figure 3. Raman spectra of: (a) The as deposited W-W₃O films, (b) irradiated zone and (c) monoclinic WO₃ crystalline powder

4. Conclusions
In this work we showed evidence of three effects that appear after pulsed laser irradiation of W-W₃O films. A modest increment of the oxygen content in the irradiated zone was identified by EDS measurements. The features of the Raman spectrum of the irradiated zone indicate that the irradiated material is a mixture of a dominant amorphous phase and a crystalline tungsten oxide. An interesting surface nano-porosity structure is developed with the pulsed laser irradiation. Such laser-induced material porosity might be useful for gas sensing applications.

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