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Formation of stoichiometric, sub-stoichiometric undoped and hydrogen doped tungsten oxide films, enabled by pulsed introduction of O_2 or H_2 during hot-wire vapor deposition

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A B S T R A C T

Tungsten oxide films with various stoichiometries, undoped and hydrogen doped were deposited by heating a W wire at 660 °C and at a base pressure of 13 Pa set by various gasses (O_2, N_2, H_2) or gas mixtures (N_2–O_2 10% in O_2, forming gas, FG) and pulsed injection of O_2 or H_2. Using this method and dependent on the deposition conditions four classes of hot-wire (hw) tungsten oxide films were synthesized: i) stoichiometric (hwWO_3), ii) oxygen deficient (sub-stoichiometric, hwWO_x with $x < 3$), iii) stoichiometric and hydrogen doped (hwWO_3:H), and iv) sub-stoichiometric and hydrogen doped (hwWO_x:H). Due to the pulsed injection of O_2 the W wire re-oxidizes during deposition thus creating WO_3 vapors continuously, so films deposited by this method do not suffer by thickness limitations and, moreover, exhibit high porosity. The optical properties of these classes of films, studied with spectroscopic ellipsometry (SE) measurements, differ substantially between them indicating corresponding differences in their electronic structures. So, hwWO_3 films were semiconducting exhibiting a band gap near 3 eV. Sub-stoichiometric hwWO_x deposited with up to 2 injections of O_2 were semi-metallic preserving some features of the electronic structure of the pure metal, while further injection of O_2 leads to stoichiometric films. Fourier transform infrared spectroscopy and SE measurements indicated that hwWO_x films contain H bonded with the O ions while in hwWO_3:H and hwWO_x:H the H is incorporated in films by direct bonding with the W ions.

1. Introduction

Since the beginning of the development of electron beam-based instruments, it was observed that by heating a tungsten filament in vacuum, a thin conducting layer is deposited on the internal walls exhibiting very good step coverage and conductivity depending on chamber pressure; decreasing with it. This layer is formed from the evaporation of the (native) tungsten oxide formed on the filament whose vapor pressure is higher than that of the metal over a wide range of temperatures [1]. Also, other refractory metal oxide films (hot-wire, hw, vapor deposited metal oxide, hwMO, films), such as of Mo and of Ta, have been deposited by this method [2–4]. In recent years hwMO films of W and Mo, deposited at filament temperatures above 1100 °C have attracted considerable attention because features, such as columns, tubes, and needles, with dimensions in the nanoscale [5–15] were found in them. Also, nano-structured hwWO_3 films were used in electrochromic devices of high performance [16,17]. In a previous work [1] it was shown that at lower filament temperatures, up to 900 °C, and pressure of 13 Pa of N_2, ultra-porous, highly transparent, stoichiometric hwWO_3 films were deposited with refractive index as low as 1.2 within the visible range. At similar filament temperatures and partial pressure of 1.3 Pa of H_2, oxygen-deficient (sub-stoichiometric) hwWO_x ($x < 3$) layers were obtained exhibiting semi-metallic properties as shown by studying their optical and electrical properties [18].

As noted above, hot-wire tungsten oxide films with stoichiometry dependent on the deposition environment are deposited by the condensation on the substrate of the vapor formed by the sublimation of the superficial native oxide present on the metallic filament [1,18]. Therefore, the deposition rate decreases with time and practically vanishes once all the superficial native oxide on the metallic filament volatilizes, so this deposition method is limited for rather thin films. For the case of stoichiometric hwWO_3 films, the introduction of O_2 into the chamber during deposition, to re-oxidize the filament and obtain thicker films, causes the production of dust which falls on the substrate while the produced layers exhibit poor adhesion and homogeneity (unless very short deposition times of the order of 1–2 s are used). For sub-stoichiometric, hwWO_x, films deposited in H_2 environment, introduction of O_2 also yielded fully oxidized samples of

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unacceptable quality. To overcome the above drawbacks we designed a deposition system, in which small quantities of O_2, are injected in the reactor using atomic layer deposition (ALD) valves with a response time of 50 ms. In this way the hot W filament is rapidly oxidized and tungsten oxide vapors are produced following the O_2 pulse, so the deposition continues and thicker tungsten oxide films are obtained. Similarly, H_2 was injected and it was found that the deposited films were doped with protons producing a family of $hwWO_x$ films ($hwWO_x$:H, $x \leq 3$). Using this system then, four kinds of hot-wire tungsten oxide films were synthesized: Stoichiometric ($hwWO_3$), sub-stoichiometric ($hwWO_x$, $x < 3$), stoichiometric and H doped ($hwWO_3$:H) and sub-stoichiometric and H doped ($hwWO_x$:H, $x < 3$). The morphology of these films obtained by scanning electron microscopy (SEM) and their optical properties studied by spectroscopic ellipsometry (SE) and Fourier transform infrared (FTIR) measurements are described in this work.

2. Experimental details

The deposition system used in this study is schematically shown in Fig. 1. It consists of a stainless steel reactor in which the sample is positioned on an aluminum susceptor 2 cm below a tungsten filament heated by an (AC) current lead by two Cu leads. The filament temperature was controlled by the current using calibration data obtained with a tiny thermocouple mechanically fixed on it. All depositions in this work were made with a filament temperature of 660 °C. The base pressure was set at the desired point by a commercial system containing a diaphragm pressure gage (Baratron) and a PC-driven needle valve allowing for the flow of (one of) various gasses such as O_2, N_2, H_2 or forming gas (FG, a mixture of H_2–N_2, 10% in H_2) through the reactor thus setting the deposition environment. The same PC also drives the atomic layer deposition (ALD) and the various shut-off valves. The ALD valves and the associated gas lines (containing valves and tubing not shown in Fig. 1) are heated, allowing for the injection of a variety of precursors into the reactor. It is seen then that the system is actually a hot-wire ALD system but in this work the filament played the role of the precursor, the deposition ambient was set by a gas flow (of O_2, N_2, H_2 or FG) and O_2 or H_2 was injected during deposition through the two ALD valves. It is also noted that mainly N_2 and FG were used for setting the deposition ambient. Pure O_2 was used for a limited number of samples only, which were used for the FTIR analysis, since the corresponding films were of unacceptable quality (see above). H_2 and FG gave very similar results so the latter was preferred because its use is safer.

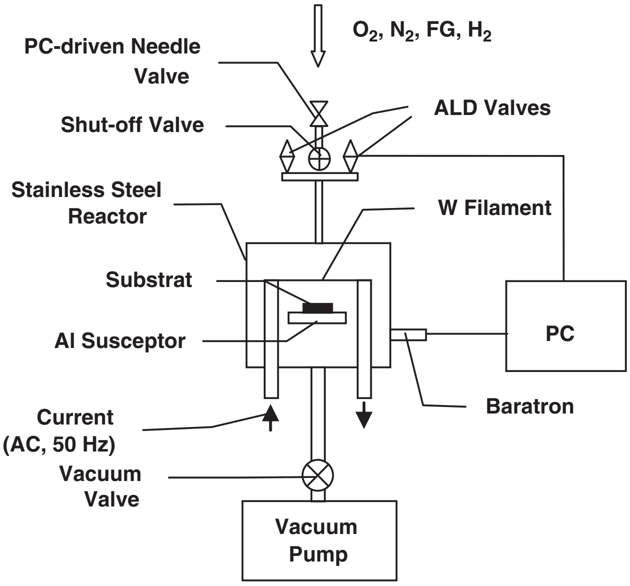

Fig. 1. Schematic representation of the HWALD system used in this study.

Depositions were carried out on Si pieces with dimensions of 2 × 2 cm^2 cut from (100) Si wafers. Prior deposition substrates were given a piranha clean [19], washed in ultra-pure water and dried in a nitrogen stream.

For the deposition, after loading the substrate, the system was evacuated down to 1.3 Pa. Then, the base pressure was set to 13 Pa and the W wire was turned on. Depositions were carried out without O_2 or H_2 pulsed injection, yielding results identical to previous works [1,18], and by injecting pulses of the above gasses at various time rates and peak pressures (results in this work refer to peak pressures of 105 Pa lasting approximately 1 s).

As shown below, the deposition time, the number of O_2 pulses and the total duration of the deposition influence film thickness. Due to the relatively short deposition times and the high thermal mass of the aluminum susceptor, the substrate temperature was remaining near room temperature during deposition. After turning-off the filament, samples were left to cool down to room temperature while the base pressure (deposition ambient) was maintained. The cooling down was enduring several minutes.

SE measurements were made within the 350–1000 nm range using a J.A Woolam Inc. M2000F rotating compensator ellipsometer (RCE™) running the WVASE32 software at an angle of incidence of 75.14°. A LEO Supra 35 was used for SEM measurements. FTIR spectroscopy measurements (in absorption mode) were made using a Bruker spectrometer.

3. Results and discussion

3.1. Stoichiometric $hwWO_3$ films deposited in N_2 environment and injection of O_2

In Fig. 2 the evolution of thickness with total deposition time is depicted for films deposited in N_2 ambient for: a) no O_2 injection [1], b) injection of one O_2 pulse after 5 s of turning on the filament and c) two O_2 pulses injected at 5 and 15 s after turning on the filament. As shown previously [1] in N_2 ambient, stoichiometric, $hwWO_3$, films are obtained. The deposition time is defined as the total deposition time shown in figure minus the time at which the last O_2 pulse was injected into the chamber. For instance, the deposition time of the sample at the right upper corner in Fig. 2 is 15 s (i.e., 30 s, total deposition time read on the x axis, minus 15 s, the moment the second O_2 pulse was injected). It can be observed that every O_2 pulse causes a jump to the thickness vs total deposition time variation by approximately

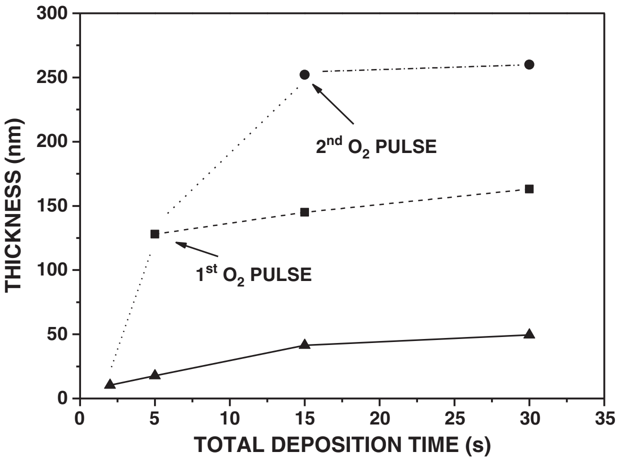

Fig. 2. Evolution of thickness of $hwWO_3$ films with the injection of O_2 and the total deposition time. Data without O_2 injection (triangles) are taken from Ref. [1]. The short-dotted line is only a guide to the eye.