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Structure, composition and electronic transport properties of tungsten oxide thin film sputter-deposited by the reactive gas pulsing process

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HIGHLIGHTS

- Tunable tungsten oxide thin films are produced by reactive sputtering.
- The Reactive Gas Pulsing Process is used to adjust WO_x properties.
- A gradual transition of WO_x from metallic-to-insulating behavior is measured.
- Gas pulsing allows an accurate control of oxygen content and conductivity.

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ABSTRACT

Tungsten oxide thin films were prepared by DC magnetron sputtering. The reactive gas pulsing process was implemented to modify tungsten and oxygen concentrations in the films. A rectangular pulsing signal was used with a pulsing period fixed at $P = 16$ s, whereas the duty cycle α was systematically changed from $\alpha = 0–100\%$ of P. The chemical composition of the films showed a gradual increase of oxygen-to-tungsten concentrations ratio from 0 to more than 3.0 as a function of the duty cycle. Films became poorly crystallized and even amorphous with an increase of the oxygen content. Similarly, a typical columnar structure was observed for pure or oxygen-rich tungsten films, which vanished when the duty cycle was higher than a few % of P. The optical transmittance in the visible range of WO_x films deposited on glass also showed a progressive change from absorbent to transparent as the duty cycle was increased. Electronic transport properties including conductivity, carrier mobility and concentration also demonstrated the controlled and regular evolution of the electrical properties from metallic to insulator when the duty cycle and thus oxygen concentration in the films changed from pure tungsten to over-stoichiometric WO_3 compound.

1. Introduction

For the last decades, numerous binary metal oxide thin films have been produced by reactive sputtering since this process is an attractive way to efficiently prepare semi-conducting and dielectric materials [1–5]. There has been a continuous improvement towards fabricating tunable oxide coatings playing with the deposition parameters. Among the large panel of binary oxides, the growth and characterization of tungsten-based compounds have extensively been studied due to their remarkable optical, electrical and chemical properties [6–8]. Thus, these tungsten oxide films have been used in various fields of applications such as antireflective and electrochromic coatings [9], gas sensors and catalysts [10] and so on. However, most of the reported investigations has been focused on stoichiometric WO_3 or oxygen-deficient WO_3 thin films [11,12]. A few studies have been devoted to the behaviors of WO_x thin films with a wide range of oxygen concentrations, i.e. $0 < x < 3.0$ [13]. This lack of knowledge is even more significant for tungsten oxide thin films prepared by reactive sputtering. Basically, when a metallic target like tungsten is sputtered in a reactive atmosphere (e.g. argon + oxygen gases), the process abruptly drops in a reactive mode as the oxygen mass flow is increasingly supplied [14]. This typical nonlinear effect of the reactive sputtering process

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restrains the range of reachable compositions. Thus, it may become a challenge to accurately change the oxygen and tungsten elemental concentrations in the films without using feedback control systems or high pumping speeds [15–17]. Recently, the Reactive Gas Pulsing Process (RGPP) [18] was developed to deposit metal oxide thin films with tunable compositions. It was successfully used to reach titanium, niobium, tantalum, iron, zirconium and tungsten oxide and oxynitride thin films with a wide range of metalloid contents [19–25]. All these investigations support that RGPP is not only an exciting method, which was developed to deposit tunable and homogeneous ceramic thin films, it can also be involved to get periodic multilayered structures of oxide/nitride, oxynitride/oxide, *etc.* at the micro- and nanoscale. Consequently, RGPP does not solely provide an added-value for better controlling the reactive sputtering process, it also appears as an original method to precisely adjust compositions and resulting properties of metal oxide thin films prepared by reactive sputtering.

In this article, we report on the deposition of tungsten oxide thin films prepared by reactive sputtering. The RGPP is implemented to produce adjustable oxygen and tungsten atomic concentrations in the films. The strategy consists in pulsing the oxygen gas during the sputter deposition, in order to alternate the process between metallic and oxidized sputtering modes and thus to get various WO_x compounds from metallic W to WO_3 compounds. The injection time of the oxygen gas is systematically changed, so as to reach a regular and well-controlled evolution of the growth rate, composition, optical behaviors and electronic transport properties. A gradual transition from metallic to insulating behaviors is finally demonstrated and connected to a single pulsing parameter, namely the duty cycle, and thus to the oxygen concentration in the films.

2. Experimental details

Tungsten oxide thin films were produced by DC reactive magnetron sputtering system in a 40 L vacuum chamber [26]. Before depositing, an ultimate pressure of 10^{-5} Pa was reached with a turbo pump backed by a mechanical pump. A 2-inch disk tungsten target (purity 99.9 at. %) was sputtered using a constant current density $J_W = 50$ Am^{-2} and the target-to-substrate distance was maintained at 60 mm. The magnetic field strength (about 600 Gauss) parallel to the target surface of the magnetron system was produced by permanent magnets (FeNdB). Argon gas was injected with a mass flow rate of 1.2 sccm (standard cubic centimeters per minute, 273 K and 1 atm.), and the pumping speed was kept at 13 Ls^{-1} corresponding to a constant argon partial pressure of 0.3 Pa. The oxygen gas mass flow rate was pulsed *vs.* time by means of the Reactive Gas Pulsing Process (RGPP) [27]. A rectangular pulsing signal was used as shown in Fig. 1. The t_{ON} time of the rectangular pulse was systematically changed from 0 to 100% of the pulsing period $P = t_{ON} + t_{OFF}$. The pulsing period P was fixed at 16 s. This procedure allows a gradual variation of the duty cycle defined as $\alpha = t_{ON}/P$ from 0 to 1 (i.e. 0–100% of P). The maximum and minimum oxygen flow rate $q_{O2\ Max}$ was set at 2.4 sccm during the t_{ON} time. This value corresponds to the oxygen amount required to completely avalanche the reactive sputtering process in the oxidized sputtering mode. During the t_{OFF} time, the oxygen mass flow rate was completely stopped (0 sccm). For all films, the deposition time was adjusted in order to get a thickness of 500 nm. It was measured with a profilometer Alpha-step IQ, KLA-Tencor Corporation. Tungsten oxide films were deposited on glass and (100) silicon substrates (surface area of 1.25 × 2.5 cm^2 for each one). Before depositing, all substrates were ultrasonically cleaned with acetone, ethanol and ultrapure water for 10 min and finally dried in an oven at 60 °C.

Optical transmittance spectra of thin films deposited on glass substrate were recorded with a UV/Vis/NIR spectrometer (Lambda 900 Perkin Elmer instruments). X-ray diffraction (XRD) patterns of the films were recorded by a BRUKER D8 focus diffractometer using monochromatized Cobalt source ($\lambda_{K\alpha} = 1.78897$ Å) according to a Bragg–Brentano θ-2θ configuration and a LynxEye linear detector. Scan was performed with a 2θ angle ranging from 20 to 80°. The energy dispersive X-ray spectroscopy (EDS) analyses were carried out with a EDAX system (FEI Quanta 450), in order to determine oxygen and tungsten concentrations in the films. Scanning election

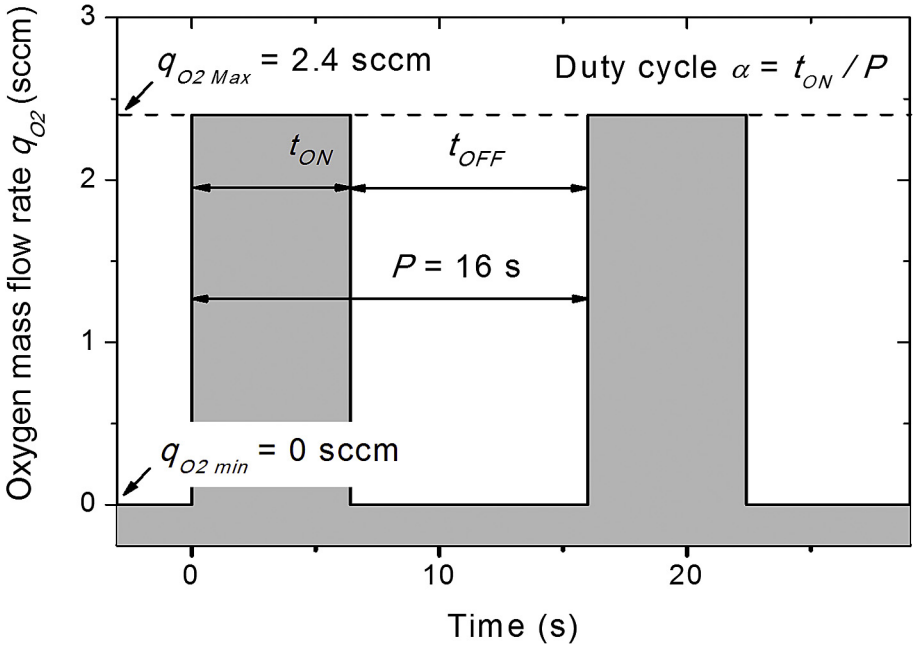

Fig. 1. Schematic representation of oxygen mass flow rate *vs.* time used for depositing tungsten oxide thin films by the reactive gas pulsing process. Pulsing period P, minimum $q_{O2\ min}$ and maximum $q_{O2\ Max}$ oxygen flow rates were kept constant at 16 s, 0 sccm and 2.4 sccm, respectively. The duty cycle α defined by the t_{ON} time-to-period ratio was systematically changed from 0 to 100% of $P = t_{ON} + t_{OFF}$.