

# Properties and electrochromic performances of reactively sputtered tungsten oxide films with water as reactive gas

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## Abstract

A change of water vapour partial pressure from 0 to 4 Pa was carried out in order to prepare sputtered tungsten oxide compounds with various oxygen and hydrogen concentrations. Oxygen, tungsten and hydrogen concentrations were determined by Rutherford Backscattering Spectroscopy (RBS) and by Elastic Recoil Detection (ERD) analysis. Structure of tungsten oxide films was analyzed by X-ray diffraction. At low water vapour partial pressure, the films are crystallized and WO<sub>2</sub> and W<sub>3</sub>O phases were observed. The electrochromic performances of such film/SnO<sub>2</sub>/glass substrate system were measured and discussed taking into account the influence of the water vapour partial pressure injected into the deposition process on the structure, chemical composition and optical properties of the films.

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## 1. Introduction

Transition metal oxides have been studied with respect to their electrochromic properties for applications as smart windows, antireflecting mirrors and display devices [1,2]. Since the discovery of the electrochromism phenomenon [3,4], electrochromic layers based on WO<sub>3</sub> have been the most widely investigated oxide in the past.

WO<sub>3</sub> is a cathodic electrochromic material in which the coloration mechanism (from transparent to blue) is generated by the electrochemical reduction. This mechanism is promoted by cathodic polarization, which caused ion insertion and electron injection. The injected electrons are trapped by some W<sup>VI</sup> sites forming W<sup>V</sup> sites, and ions remain ionized in the interstitial sites of the expanded WO<sub>3</sub> lattice. This double injection into the film of WO<sub>3</sub> induces the formation of the tungsten bronze (H<sub>x</sub>WO<sub>3</sub>) having electronic structure, electrical and optical properties changed in comparison with

single tungsten oxide. Thin films of WO<sub>3</sub> can be prepared by different techniques. Sputtering is one of the most widely used techniques because high-quality films are obtained with higher composition reproducibility. To the best of our knowledge, no study has been devoted to the synthesis of WO<sub>3</sub> films by sputtering methods using water as reactive gas. The introduction of hydrogen-bearing species in the growth process provides the possibility to modify the W valence and to change the transport and electrochromic properties of sputtered-deposited WO<sub>3</sub> films.

In this paper, we report on the use of water vapour as reactive gas to deposit tungsten oxide films. A survey on the effect of water vapour partial pressure on some process parameters is studied first. Structural and chemical composition changes in relation to the optical and electrochromic properties are finally discussed.

## 2. Experimental

A tungsten target (purity: 99.95%, 50 mm diameter) was DC sputtered with a constant current density  $J_W=20 \text{ A m}^{-2}$ .

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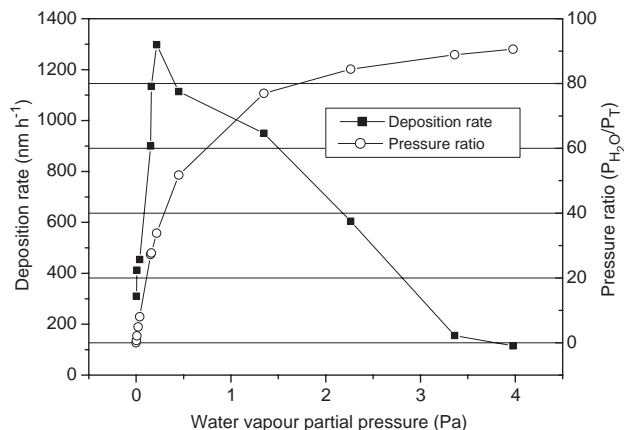


Fig. 1. Deposition rate of tungsten oxide films and pressure ratio vs. water vapour partial pressure at 293 K.

Argon was introduced first up to a pressure  $P_{Ar}=0.4$  Pa (constant pumping speed  $S=10$  L s<sup>-1</sup>). Afterwards, the water vapour partial pressure ( $P_{H_2O}$ ) was changed from 0 to 4 Pa using a leak valve connected to a de-ionised water flask. The pressure ratio ( $R_{H_2O}$ ) is defined by  $R_{H_2O}=P_{H_2O}/P_T$ .

The crystallographic structure was investigated by X-ray diffraction using Cu K $\alpha$  radiation ( $\lambda=1.5406$  nm) at a grazing angle incidence  $\theta=1^\circ$ . Optical properties were analysed from optical transmittance spectra of the film/glass substrate system.

Nuclear elemental analyses were performed with ALTAIS, the 2 MV Tandem accelerator installed at LARN. Typical nuclear reactions induced by  $\alpha$ -particles were used to measure elemental composition. The experimental details for nuclear analysis have been presented in previous papers [5,6].

The electrochemical measurements were performed using a Tacussel model PGP201 potentiostat and voltmaster 1 pilot software with a three electrodes configuration in a 1.0 M H<sub>2</sub>SO<sub>4</sub> solution. The working electrode was glass/SnO<sub>2</sub>:F (25  $\Omega/\square$ )/WO<sub>x</sub>H<sub>y</sub> film. A platinum disk and a SCE (Standard Calomel Electrode) were used as auxiliary and reference electrodes, respectively. Cyclic voltametry was carried out at a rate of 500 mV min<sup>-1</sup> and potentiostatic intermittent experiments at voltages between -1.0 to 2.5 V/SCE. The optical density change is defined as  $\Delta OD=\log(T_b/T_c)$  where  $T_b$ =transmission at 632 nm for the bleached state and  $T_c$ =transmission at 632 nm for the coloured state. The coloration efficiency (CE) was calculated from the charge density  $Q_c$  (C m<sup>-2</sup>) inserted during the step coloration and calculated according to the following equation  $CE=\Delta OD/Q_c$ .

### 3. Results and discussion

#### 3.1. Process

Deposition rate exhibits a maximum (1300 nm h<sup>-1</sup>) for  $R_{H_2O}$  close to 35% (Fig. 1), which corresponds to  $P_{H_2O}=0.3$

Pa. Similar results have been obtained by Kaneko et al. [7] and Yamamoto et al. [8] for the deposition of tungsten oxide using O<sub>2</sub> as reactive gas. The evolution of the target potential as function of  $P_{H_2O}$  can be explained by the change of sputtering mode. Oxidation rate at the target predominates on the sputtering rate. The difference of molar volumes of components deposited on the substrate can explain the rise of deposition rate if the number of W atoms impinging on the surface is the same. For further increase of  $P_{H_2O}$ , the target potential exhibits a drop and reaches a minimum value close to  $U_w=390$  V. It probably correlates with an oxidised state of the target. Then, the W–Ar–H<sub>2</sub>O process trapped in the oxidised sputtering mode (sputtering yield of tungsten oxide lower than that of metallic tungsten) and the deposition rate decreases from 1300 to 1100 nm h<sup>-1</sup>. Such a decrease may indicate that the target poisoning starts at low  $R_{H_2O}$  and spreads out above 75%. However for ratio higher than 90%, the deposition rate is almost constant, which probably corresponds to a fully oxidised state of the surface of the target. These results reveal that the amount of water vapour required to change the process to oxidised sputtering mode is high because transition is close to  $P_{H_2O}=1.5$  Pa ( $R_{H_2O}=80\%$ ). Also, the target potential can be used as a key parameter to

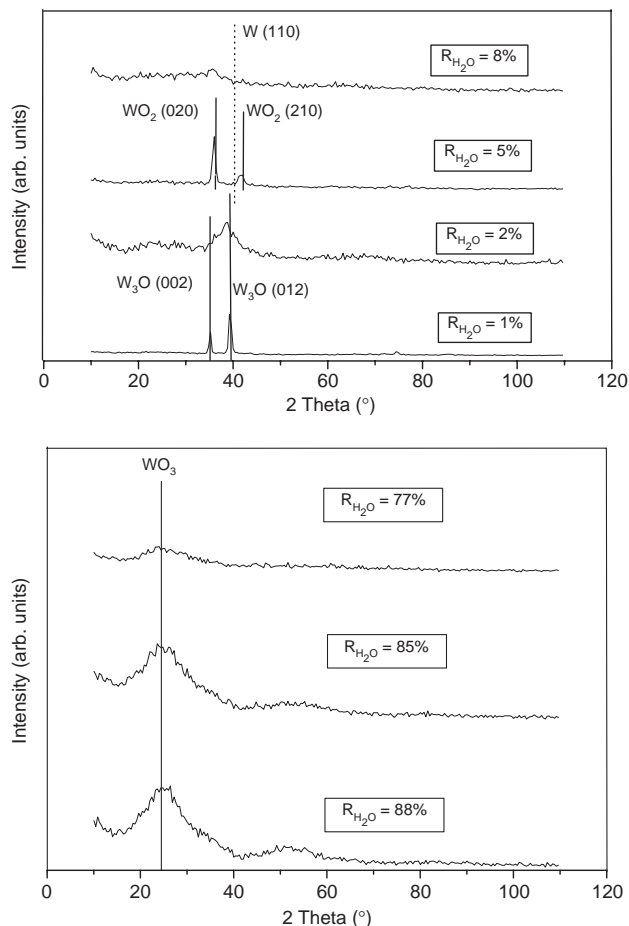


Fig. 2. X-ray diffraction patterns of tungsten oxide films deposited on glass substrate at 293 K for different water vapour pressure ratios.

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