



# Tungsten oxide thin film exposed to low energy He plasma: Evidence for a thermal enhancement of the erosion yield



H. Hijazi <sup>a</sup>, Y. Addab <sup>a</sup>, A. Maan <sup>b</sup>, J. Duran <sup>b</sup>, D. Donovan <sup>b</sup>, C. Pardanaud <sup>a</sup>, M. Ibrahim <sup>a</sup>, M. Cabié <sup>c</sup>, P. Roubin <sup>a</sup>, C. Martin <sup>a,\*</sup>

<sup>a</sup> Aix-Marseille Université, CNRS, PIIM UMR 7345, F-13397 Marseille, France

<sup>b</sup> University of Tennessee-Knoxville, 1004 Estabrook Road, Knoxville, TN, 37996-2300, USA

<sup>c</sup> Aix-Marseille Université, CP2M, F-13397 Marseille, France

## ARTICLE INFO

### Article history:

Received 9 September 2016

Accepted 30 November 2016

Available online 1 December 2016

### Keywords:

Tungsten oxide thin film

He plasma bombardment

Erosion

Plasma wall interaction

Raman spectroscopy

Transmission electron microscopy

## ABSTRACT

Nanocrystalline tungsten oxide thin films (about 75 nm in thickness) produced by thermal oxidation of tungsten substrates were exposed to low energy He plasma ( $\approx 20$  eV/He) with a flux of  $2.5 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$  at two temperatures: room temperature and 673 K. The structure and morphology modifications which occur after this He bombardment and annealing treatments was studied using Raman spectroscopy and transmission electron microscopy. Due to the low fluence ( $4 \times 10^{21} \text{ m}^{-2}$ ) and low ion energy, we have observed only few morphology modifications after He plasma exposure at room temperature. On the contrary, at 673 K, a change in the layer color is observed associated to an important erosion. Detailed analyses before/after exposure and before/after annealing allow us to describe the He interaction with the oxide layer, its erosion and structural modification at the atomic and micrometer scale.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Because of its favorable physical properties, such as a high melting point and an excellent erosion resistance, tungsten (W) is being used as plasma facing component (PFC) material for magnetic fusion devices such as the tokamaks ASDEX-Upgrade [1], ITER [2], JET [3] and WEST [4]. During the deuterium-tritium (D–T) fusion operation of ITER, significant helium (He) ash will be formed and will interact with the W divertor. Under plasma divertor conditions and even for impact energies below the physical sputtering threshold, which is estimated around 300 eV [5], He ions have been found to cause erosion and redeposition or codeposition as well as significant morphology changes in W [6–10]. It should be noted that He ion bombardment has been found to have high affinity to create bubbles, holes and nanostructures. These damages will change W physical and mechanical properties and this will change their interaction with plasma (such as: erosion rate, implantation and diffusion depth).

Various types of mixed materials can be formed during

redeposition and codeposition processes in presence of impurities [11]. Oxygen can exist as contamination in tokamak vacuum vessels and W PFCs can be oxidized, this process being facilitated by the high temperatures reached during operation of the machine. Tungsten oxide can therefore be formed at the surface of tokamak PFCs with various stoichiometries [11,12], the most stable being  $\text{WO}_3$ , whose behavior in the tokamak environment is still not well known. Basically the tungsten oxide crystal  $\text{WO}_3$  is built up from corner-sharing  $\text{WO}_6$  octahedra, it easily forms substoichiometric shear phases ( $\text{WO}_{3-x}$ ) containing edge-sharing octahedra with various crystallographic structures.

Although many studies have been concerned with the consequences of He and D bombardments on W [5–10], only a few works have explored the behavior of  $\text{WO}_3$ . The presence of an oxide layer can reduce the sputtering energy threshold of W by a factor of 10, increase the erosion yield [13] and generate different hydrogen isotope retention mechanisms [14–16]. A. Pezzoli et al. [17] produced  $\text{WO}_3$  layers by the pulsed laser deposition technique in order to simulate redeposited layer compounds that can be present on PFCs. They have shown that the layer morphology and stoichiometry can be controlled by changing background  $\text{O}_2$  pressure during deposition. Surface modifications, such as nano-cracks, pinholes and bubbles, were observed after high flux ( $10^{24} \text{ m}^{-2} \text{ s}^{-1}$ ) D plasma

\* Corresponding author.

E-mail address: [celine.martin@univ-amu.fr](mailto:celine.martin@univ-amu.fr) (C. Martin).

exposure in Magnum–PSI at a layer temperature of 580 K [17]. Another study of tungsten oxide layers grown on polycrystalline ITER-grade surfaces by annealing in air for 10 min was carried out at various sample temperatures [18]. It has been shown that at low-energy (38 eV/D) and high flux ( $10^{22} \text{ m}^{-2} \text{ s}^{-1}$ ) D plasma exposure (fluence of  $10^{26} \text{ m}^{-2}$ ), the formation of cracks appears for temperatures above 605 K.

In a previous study, we have observed a color change and a phase transition of  $\text{WO}_3$  layers due to the formation of tungsten bronze ( $\text{D}_x\text{WO}_3$ ) after a low energy ( $\approx 20 \text{ eV}$ ) and low fluence ( $4 \times 10^{21} \text{ m}^{-2}$ ) deuterium plasma exposure at room temperature [19]. This structural modification is due to D intercalation and deep diffusion into the  $\text{WO}_3$  channels and is reversible after a few days at ambient conditions.

In this work, the structural changes of  $\text{WO}_3$  layers under low energy ( $\approx 20 \text{ eV}$ ) and low fluence ( $4 \times 10^{21} \text{ m}^{-2}$ ) He plasma exposure at room temperature and 673 K was studied with the help of Raman spectroscopy and transmission electron microscopy. Our results emphasize an important effect of the sample temperature on these structural changes.

## 2. Experimental

### 2.1. $\text{WO}_3$ thin film production

Polycrystalline recrystallized tungsten (pc-W) samples produced by A.L.M.T. Corp., Japan (purity of 99.99%), measuring  $7 \times 7 \times 0.3 \text{ mm}$ , were used as substrates for growing oxide layers. The W grain size was found to be a few tens of micrometers using scanning electron microscopy (SEM) (Microscope Philips XL30 SFEQ, Schottky Field Emission Gun). The pc-W substrates were outgassed at  $10^{-7}$  torr and 673 K during 4 h. Afterwards, thermal oxidation at 673 K on the pc-W substrates was performed at oxygen pressure of 590 torr during 90 min. Thanks to this procedure, we produced a set of identical  $\gamma\text{-WO}_3$  (referred to  $\text{WO}_3$  hereafter) samples whose structure was monoclinic and nanocrystalline, as confirmed by X-rays diffraction analysis (not shown in this paper). The oxide layer thickness, measured using a FIB cross-section technique (FEI Helios 600 NanoLab Dual Beam), was about  $75 \pm 4 \text{ nm}$ . The corresponding oxide layer color was blue.

Raman spectra were recorded using a Horiba-Jobin-Yvon HR LabRAM microscope ( $\lambda = 514 \text{ nm}$  and  $532 \text{ nm}$ , laser spot size  $\approx 1 \mu\text{m}^2$ ). The laser power was kept at about  $1 \text{ mW } \mu\text{m}^{-2}$ . The Raman mapping mode was used to average 30 spectra collected over a  $750 \mu\text{m}^2$  area in order to increase the signal to noise ratio and to detect eventual inhomogeneities. Spectra were measured in the Raman shift range of  $100\text{--}1250 \text{ cm}^{-1}$ . Transmission Electron Microscopy (TEM) (FEI Tecnai G2 – thermo-ionic  $\text{LaB}_6$  electron source – accelerated voltage 200 kV) was used for the structural analysis of the oxide layer and oxide/tungsten interface on  $\sim 100 \text{ nm}$  slices cut perpendicular to the sample surface by Focused Ion Beam (FIB) technique.

### 2.2. Plasma exposure stage

The University of Tennessee Nuclear Engineering (UTNE) ion exposure stage utilizes a PCS-ECR Plasma Cracker Source manufactured by SPECS Surface Nano Analysis GmbH, which is a compact electron cyclotron resonance (ECR) ion source (Fig. 1) [20]. This experiment is similar in design and purpose to the ion exposure stage utilized at Sandia National Laboratory, which demonstrated the capability to produce He bubble growth in heated W samples using a compact ECR ion source [21]. The UTNE source operates with helium or other inert gases and is equipped with a molybdenum extraction grid able to be biased up to  $-1000 \text{ V}$  to accelerate

the ions to the desired energy. The He ion flux used during exposures was kept at approximately  $2.5 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$  at the sample face (with a corresponding current  $\approx 20 \mu\text{A}$ ). The W samples were mounted on a pyrolytic boron nitride (PBN) plate heater manufactured by Momentive Performance Materials, which was capable of heating samples to temperatures up to approximately 1300 K.

The sample was held in place on the heater stage with the PBN plate that also controlled the exposed area (Fig. 2). The sample holder was mounted on a linear motion vacuum feedthrough in the sample loading chamber. The sample loading chamber could then be sealed and pumped down to several millitorr, allowing the gate valve separating the plasma exposure chamber and the sample loading chamber to be opened. The linear motion feedthrough then allowed the sample to be inserted into the ion exposure chamber and brought to within 4 cm of the exit aperture of the ion source.

The base pressure in the ion exposure chamber was about  $2.2 \times 10^{-5}$  torr before the exposure. In the case of the exposure at 673 K, the sample was heated up slowly during 90 min to reach 673 K with a pressure in the chamber around  $1.3 \times 10^{-5}$  torr, remaining at around  $9.4 \times 10^{-4}$  torr during the exposure at room temperature and 673 K. Table 1 summarizes the experimental conditions the four identical  $\text{WO}_3$  layers: (i)  $\text{WO}_3$  as oxidized was used as a reference, (ii)  $\text{WO}_3$ -673 K was annealed in a vacuum chamber at 673 K during 2 h at  $7.5 \times 10^{-6}$  torr, (iii)  $\text{WO}_3$ -HeRT and (iv)  $\text{WO}_3$ -He673 K were exposed to 20 eV He plasma with a fluence of  $4 \times 10^{21} \text{ m}^{-2}$  (exposure time of 27 min) at room temperature and 673 K, respectively.

## 3. Results and discussions

### 3.1. Annealing effect

Fig. 3 shows the Raman spectra of as oxidized  $\text{WO}_3$  ( $\text{WO}_3$ , in blue) and  $\text{WO}_3$  annealed at 673 K ( $\text{WO}_3$ -673 K, in red) in the  $100\text{--}1100 \text{ cm}^{-1}$  region and normalized to the intensity of the main peak at  $807 \text{ cm}^{-1}$ . In the literature, the monoclinic structure is identified by two bands peaking in the range  $700\text{--}720 \text{ cm}^{-1}$  and  $805\text{--}808 \text{ cm}^{-1}$  in the stretching mode region ( $500\text{--}900 \text{ cm}^{-1}$ ) and in the range  $128\text{--}135 \text{ cm}^{-1}$  and  $268\text{--}275 \text{ cm}^{-1}$  in the bending mode region ( $100\text{--}500 \text{ cm}^{-1}$ ) [22–24]. The features found here at  $703 \text{ cm}^{-1}$ ,  $807 \text{ cm}^{-1}$  and  $130 \text{ cm}^{-1}$ ,  $270 \text{ cm}^{-1}$  confirm the monoclinic structure of the sample as previously identified by XRD. The shoulder observed at  $645 \text{ cm}^{-1}$  is attributed to oxide hydration while the shoulder observed at  $960 \text{ cm}^{-1}$  is attributed to terminal  $\text{W}=\text{O}$  stretching modes and reveals the presence of defects in the crystalline monoclinic structure. As the sample structure is nanocrystalline (see Fig. 6), these defects may be due to grain boundaries, in agreement with previous observations relating terminal  $\text{W}=\text{O}$  stretching modes to the presence of nano-grains [25]. Raman spectra of  $\text{WO}_3$  as oxidized and  $\text{WO}_3$  annealed are very similar, with no evidence for a phase reorganization: the monoclinic structure of the  $\text{WO}_3$  layer is thus clearly not modified after annealing at 673 K. The slight decrease of the shoulder at  $645 \text{ cm}^{-1}$  could be attributed to the dehydration of the  $\text{WO}_3$  layer [26,27].

Fig. 4 shows a TEM image of  $\text{WO}_3$ -673 K taken from a slice prepared by FIB. The oxide layer is compact and the tungsten/oxide interface is smooth and well defined. The layer thickness has not changed, still measured at  $75 \pm 4 \text{ nm}$  after annealing. Both the interface and the top surface (protected by a Pt coating during the FIB preparation) do not show any significant changes after annealing.

To conclude, Raman spectroscopy and TEM results show that neither the thickness nor the nano-crystalline structure of the initial  $\text{WO}_3$  layer change after a thermal treatment at 673 K.

Download English Version:

<https://daneshyari.com/en/article/5454411>

Download Persian Version:

<https://daneshyari.com/article/5454411>

[Daneshyari.com](https://daneshyari.com)