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# Impact of microwave post-deposition annealing on the crystallization of amorphous hydrogenated perovskites. The case of the three-dimensional tungsten and of the two-dimensional molybdenum oxide films

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## ABSTRACT

Hydrogenated sub-stoichiometric oxides exhibiting perovskite structure such as those of tungsten and of molybdenum ($H:MO_x$, where M = W or Mo and $x < 3$) were treated by microwave (MW) post-deposition annealing in air. The purpose of this treatment was to vibrate and therefore heat, the O—H bonds present in them only, without heating the rest of the lattice and the substrate. It was shown that, contrary to thermal heating, MW annealing did not affect significantly the oxygen and hydrogen contents in samples, but it caused an atomic rearrangement; more significant for $H:MoO_x$ than for $H:WO_x$ films, attributed to the layered, two-dimensional structure of the former contrary to the three-dimensional one of the latter. It was concluded that MW annealing at appropriately chosen frequencies may potentially be used to improve atomic ordering in other materials without causing alterations of their chemical composition and avoiding the heating of the substrate.

## 1. Introduction

Tungsten and molybdenum oxides are perovskites formed by $MO_6$ (M = W or Mo) octahedra whose centers are occupied by the metallic and the corners by oxygen ions. The lattice of tungsten oxide is made up by octahedra connected between them by sharing the corner oxygen ions [1,2], so the bond strengths along the three dimensions are comparable, therefore the material may be characterized as three-dimensional. Molybdenum oxide is two-dimensional made up by double-layers held together by weak van der Waals forces [3,4]. Each double-layer is formed by two sub-layers of $MoO_6$ octahedra laterally connected by sharing the corner ions and these sub-layers interpenetrate within each other as described in Refs. [3,4]. Protons (and light alkali ions) are easily incorporated (intercalated) within these lattices [5,6] and are stabilized near the oxygen ions forming hydroxyl radicals. In recent papers we have shown that hot-filament tungsten [7,8] and molybdenum oxide films [9,10] deposited in hydrogen environments are amorphous, sub-stoichiometric in oxygen and contain hydroxyl groups interconnected with hydrogen bonds [11]. Such films (termed hereafter as $H:MO_x$, M = W or Mo, $x < 3$) are being used in various applications such as electrochromic [12] and gaschromic windows [13], gas sensing [14] and for the modification of electrodes in organic solar cells (OSCs) [9,15,16] and light emitting diodes (OLEDs) [17–19] to facilitate injection/extraction of electric current carriers in these devices. For the latter applications, one takes advantage of properties exhibited by these hydrogenated sub-oxides such as their enhanced electrical conductivity and the ability to engineer their electronic structure by controlling oxygen sub-stoichiometry and hydrogen content [9,15–19]. In most of these applications, the crystallization of the oxide layer is desirable for reasons such as the improvement of electrical and thermal conductivity and mechanical stability, but it is prohibited by the requirement of low thermal budget imposed by the substrate, which for the above applications may be plastic, tissue or paper. Moreover, the thermal annealing of these films causes alterations to their chemical composition since heating at temperatures up to approximately 200° C causes oxygen losses, above (approximately) 400° C they start oxidizing again, while the crystallization proceeds in different ways specific for each temperature range. In any case, to obtain appreciable improvement of atomic ordering of these perovskites one needs to raise the temperature above 400° C at which temperature samples are practically fully oxidized, which for many applications may be not desirable. To overcome the high thermal budgets required to improve atomic ordering (crystallization) while maintaining stoichiometry of these hydrogenated sub-oxides, post-deposition microwave (MW) annealing was performed in ambient air at a frequency of 2.45 GHz with purpose to vibrate (and therefore heat) the O—H bonds only, without heating the rest of the lattice and the substrate. The results of this post-deposition treatment are reported here. Surprisingly, we found that the chemical composition of both kinds of

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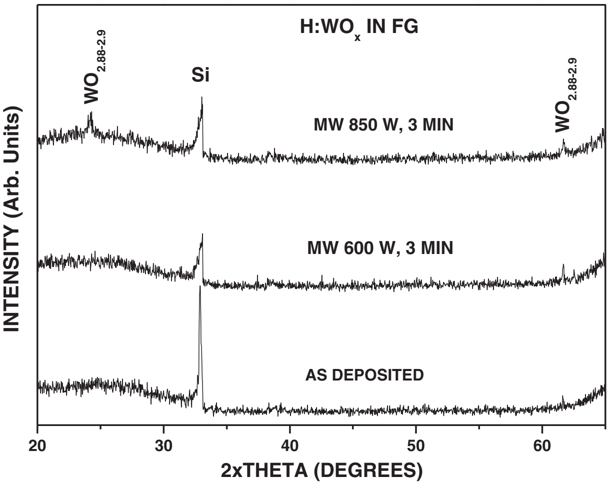


**Fig. 1.** X-ray diffraction patterns taken on an as deposited H:WO$_x$ film (lower panel) and on samples MW annealed at 3 min at 600 (middle panel) and 850 W (upper panel).

**Table 1**
Possible W—O compounds and crystallographic planes corresponding to the XRD peaks observed in Fig. 1.

| 2θ (°) | Possible compound | Crystallographic plane |
|---|---|---|
| 24.2 | $W_{19}O_{55}$ | [3 0 2] |
| | $W_{17}O_{47}$ | [5 0 0] |
| | $W_5O_{14}$ | [6 2 0] |
| | $WO_3$ | [2 0 0] |
| 61.7 | $WO_{2.92}$ | [2 2 20] |
| | $WO_{2.9}$ | [2 1 2] |
| | $W_{20}O_{58}$ | [5 1 11] |
| | $W_4O_{11}$ | [2 2 2] |

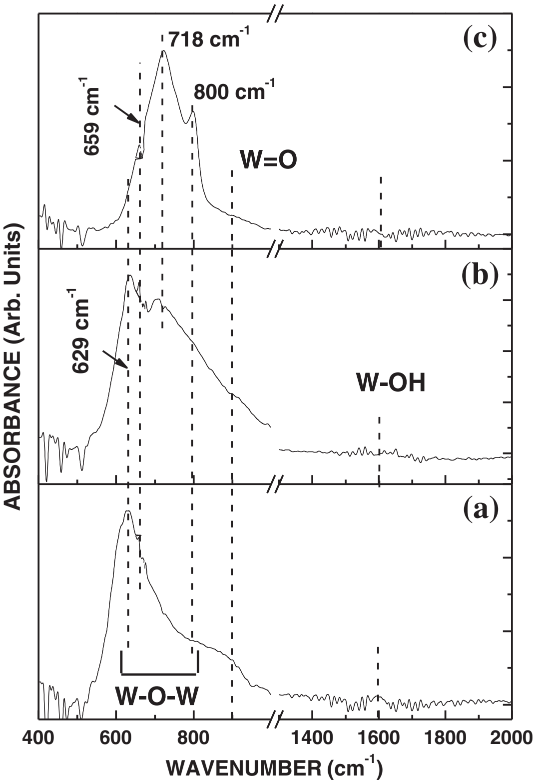
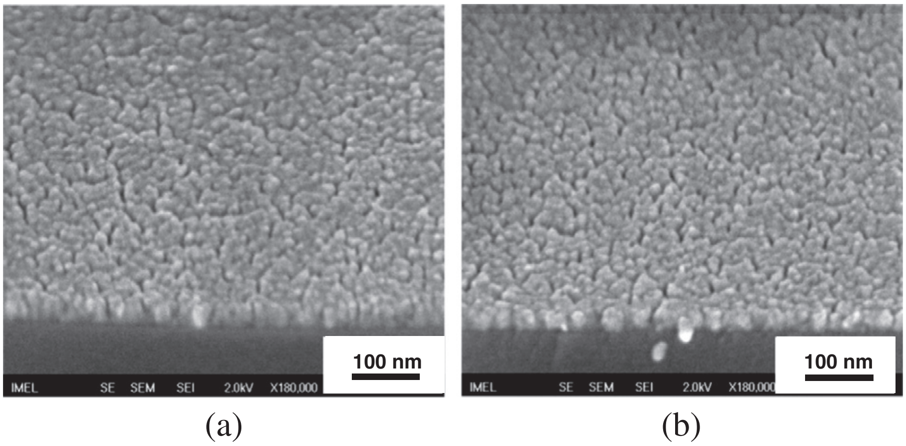


**Fig. 3.** FTIR spectra taken on three H:WO$_x$ films as deposited (a) and after post-deposition MW annealing for 3 min at 600 (b) and 850 W (c). Peaks within the range 600–800 cm$^{-1}$ correspond to vibrations of W—O—W chains [21–24] while near 1600 cm$^{-1}$ to W—OH and O—H—O.

oxide films, as determined by X-ray photoelectron spectroscopy (XPS) and optical transmission measurements, did not change with annealing. As deposited films were amorphous, i.e., bond lengths and angles were randomly distributed. After annealing, as shown by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) measurements, atomic rearrangement has taken place in films; more significant for Mo than for W oxide. In spite of improvements of short-range order (SRO) visible on the FTIR spectra, the tungsten oxide films remained to a large extent amorphous (as defined by XRD), contrary to the molybdenum oxide samples where significant improvements of crystallization were observed. The surface morphology of films, studied by scanning electron microscopy (SEM), remained almost unaffected for H:WO$_x$, while spectacular changes were observed in H:MoO$_x$ films, related to the enhancement of atomic ordering. In the results and discussion section of this work a model is presented that explores the possible ways in which the crystallization proceeds in the cases of two- and three- dimensional perovskites. The model explains the differences observed between the MW annealing induced crystallization of molybdenum and tungsten oxide films that are attributed to the two-dimensional structure of the former as opposed to the three-dimensional one of the latter. It is finally concluded that MW annealing (using MWs with appropriate frequency) may be applied for other materials to vibrate and consequently heat, specific kinds of bonds only in their lattice to obtain improvements of atomic ordering, without affecting their chemical composition and avoiding heating of the substrate.



(a) (b)

**Fig. 2.** SEM micrographs taken at a tilting angle of 65° on the surface of a 20 nm thick H:WO$_x$ sample as deposited (a) and after MW annealing at 850 W for 3 min (b).