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Sputtered WO_3 films for water splitting applications

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ABSTRACT

Tungsten oxide films with different thickness were grown by sputtering deposition. Analysis of sample morphology showed that the films were constituted by sub-micrometric columnar structures, with diameters in the range 100–500 nm. As-deposited films revealed an almost-amorphous crystal structure and a wide optical band-gap of about 3.28 eV. Thermal annealing at 500 °C was used to promote the formation of a monoclinic WO_3 crystal structure and the reduction of the band-gap. Photo-electrochemical characterizations were used to compare the responses of the different films and to evaluate their possible use in water splitting applications.

1. Introduction

Transition metal oxides are interesting materials for catalysis/photo-catalysis, electrodes, electrochemistry, etc. [1,2]. Among them, tungsten trioxide (WO_3) has been widely tested for photo-catalytic, electrochromic, gas sensing, and antibacterial applications [3–6]. In particular, WO_3 usage for water splitting applications has been strongly investigated thanks to its good photo-electron transport properties, strong resistance against photo-corrosion in aqueous solution, and optical properties. Depending on their crystal structure and quality, WO_3 films can present an energy gap below 3 eV [7], which implies a wider light absorption range than other materials commonly studied for photoelectrochemical (PEC) applications with higher energy gaps, such as TiO_2 (~3.2 eV) and ZnO (~3.37 eV) [8]. Additional enhancements can be achieved by proper modifications of WO_3-based materials in order to further extend their absorption into the visible region of the solar spectrum and to improve their transport properties, for example by doping or coupling tungsten oxide with other materials [9–10].

Since WO_3 crystal structure and optical band gap can significantly influence the material efficiency in PEC processes, it is important to adjust the WO_3 film characteristics to obtain optimal PEC response and incident photon-to-current efficiency (IPCE). To this aim, in this work WO_3 films with different thickness were sputter-deposited and characterized to evaluate their morphological, structural and optical properties. The film modifications induced by subsequent thermal annealing process were investigated. The films were then photo-electrochemically characterized by IPCE and linear sweep voltammetry, to compare their responses and find the optimal conditions for the development of WO_3-based water splitting materials.

2. Experimental

Tungsten oxide films at different thickness (100, 200, 350, and 500 nm, measured by profilometry) were deposited at room temperature by RF magnetron sputtering from a metallic W target (99.95% purity, Kurt J. Lesker). The vacuum chamber was evacuated to a base pressure of about 8×10^{-5} Pa, while the film depositions were performed in $Ar+O_2$ atmosphere at pressure of 4.5 Pa, with Ar and O_2 flows of 7 and 3.5 sccm, respectively. The RF power applied to the cathode was set at 75 W. Before starting the deposition, the target surface was sputter-cleaned for 40 min in Ar atmosphere and then for 20 min in $Ar+O_2$ atmosphere. The films were deposited onto UV-grade fused silica substrates (transparency around 90% in the range 200÷400 nm, DayOptics Inc.) for optical characterizations, and onto commercial conductive FTO-coated soda lime glass substrates (7 Ω/sq, Solaronix) in an area of 2×2 cm^2 for morphological, structural and electrochemical analyses. The samples were labeled according to the film thickness as WO_3_1 (100 nm), WO_3_2 (200 nm), WO_3_3 (350 nm),

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and WO_3_4 (500 nm). Thermal annealing at 500 °C for 2 h in air, with a heating rate of 120 °C/hour, was performed to improve the structural and optical properties of the films.

A MERLIN ZEISS high-resolution field-emission scanning electron microscope (FE-SEM), equipped with an energy dispersive analysis system (EDS), was employed in order to analyze the morphology and bulk elemental composition of the samples.

Optical transmittance (T) and reflectance (R) measurements in the wavelength range 200÷2500 nm were performed by an Agilent Cary 5000 UV–vis-NIR spectrophotometer. The spectra were corrected for the silica substrate contribution to obtain transmittance and reflectance of the tungsten oxide films. Absorption coefficient α was calculated from $\alpha = (\frac{1}{d})\ln(\frac{(1-R)}{T})$, where d is the film thickness. Tauc plots were derived from the relation $\alpha E = A(E-E_g)^2$ for indirect allowed transitions [11] (where A is a constant, E is the photon energy and E_g is the energy gap) and the optical energy gap values were obtained by extrapolating the linear fits to zero. Absorbance of the WO_3 annealed films on FTO/soda lime glass was also measured in transmittance mode, using a PerkinElmer Lambda 25 UV–vis spectrophotometer.

The structural properties of the films were studied by using a Philips MPD PW1880 X-ray diffractometer operating in parallel beam geometry and employing Cu Kα radiation ($\lambda_{CuK\alpha}$=0.154186 nm). In particular, glancing incidence X-ray diffraction (GIXRD) scans were performed with the incident X-ray beam fixed at a small angle of incidence (0.3°) while the detector was moved along the goniometer circle in the 2θ range between 20° and 90°, with a 2θ step of 0.02°.

The photo-electrochemical characterization of the annealed WO_3 films was carried out in an aqueous 0.1 M Sodium Phosphate Buffer (0.1 M, pH=7) electrolyte solution, employing a multichannel VSP potentiostat/galvanostat made by BioLogic. A three-electrode configuration, consisting of the WO_3 electrodes as working, an Ag/AgCl (3 M) as reference and a Pt wire as counter electrode, was used. Linear sweep voltammetries (LSVs) were performed at 10 mV/s in the dark and under AM 1.5G simulated solar light (at 100 mW/cm^2), using a 450 W Xe lamp by Newport with both AM 1.5 and water filters. Cronoamperometric (I–t) curves were obtained at 0.61 V *vs.* Ag/AgCl under continuous (1 min) dark–light cycles. Incident-Photon-to-Current-Efficiency (IPCE) was recorded using a Newport Xe lamp (150 W) coupled to a monochromator (Cornestone 130 by Newport), in the wavelengths range from 300 to 570 nm (step size 10 nm), at 0.6 V *vs.* Ag/AgCl. The potential *vs.* the reversible hydrogen electrode (E_{RHE}) was calculated by the Nerst equation: $E_{RHE}=E_{Ag/AgCl}+0.209\ V+0.059pH$.

3. Results and discussion

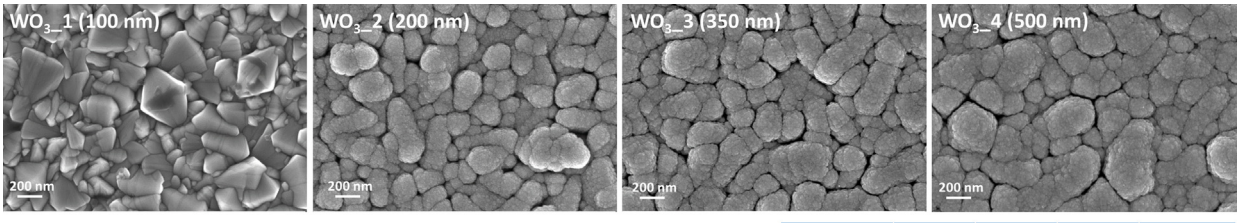
FESEM images of the surface of the as-deposited (non-annealed) films on FTO/soda lime substrates are reported in Fig. 1. The morphology of the thinnest film is due to the combination of the clusters of the tungsten oxide film and the sharp-edged crystals of the F-doped tin oxide (FTO) layer of the substrate. Then, increasing thickness from 200 to 500 nm, the deposited film evolves from round-shaped elongated particles to more circular columnar structures having diameters ranging from 100 to 500 nm, which are separated by narrow gaps of few nm. In addition, the film surface is characterized by a high roughness, with the visible presence of nanometric crystals agglomerated in big particles. From EDS analyses (see Fig. 1), it was confirmed the absence of impurities in the films, and the only presence of Sn, W and O, with an increase of the W/Sn ratio with the augmented quantity of deposited material, as expected. An exact stoichiometry of the tungsten oxide cannot be derived due to the presence of oxygen also on the substrate and to the qualitative nature of EDS measurements.

Analysis of the structural properties by GIXRD revealed that all the as-deposited films present an almost amorphous nature. The diffraction spectrum of the 200 nm-thick film, reported in Fig. 2 as representative sample, only evidences two broad bands, without any sharp WO_3 diffraction peak. The only visible diffraction peaks come from the FTO/soda lime substrate, as clearly deducible by comparison with the pattern of the bare substrate also shown in the figure. The observation of this heavily disordered structure indicated the need to process the films by a thermal annealing treatment (discussed below).

Transmittance and reflectance spectra of as-deposited films, displayed in the left column of Fig. 3, respectively show average values around 90% and 10% in the NIR-visible range and, for all films, the transmittance spectra present a cut-off wavelength below 400 nm, where the films start absorbing light.

In particular, evaluation of the film optical energy gap was obtained by plotting $(\alpha E)^{\frac{1}{2}}$, shown in the right column of Fig. 3, and fitting the linear region near the absorption edge to determine the intercept with the x-axis. Regardless of film thickness, all samples exhibit the same energy gap with a value of 3.28 ± 0.04 eV, in agreement with XRD analyses that showed very similar structure for all the samples independently of their thickness. This energy gap value is higher than crystalline WO_3 films and it is consistent with values in the range 3.2–3.4 eV observed in heavily disordered WO_3 films [7], in agreement with X-ray diffraction results.

Both structural and optical analyses indicated that films require some additional treatments for suitable testing in PEC investigations. Indeed, the almost amorphous crystal structure cannot



Elemental (Atomic %)	WO_3_1	WO_3_2	WO_3_3	WO_3_4
O	78.0	77.8	78.3	79.5
Sn	17.8	12.1	6.9	3.2
W	4.2	10.1	14.7	17.4
W/Sn	0.24	0.83	2.13	5.44

Fig. 1. (top) FE-SEM images and (bottom) representative EDS analysis with elemental atomic composition of as-deposited WO_3 films with different thickness.