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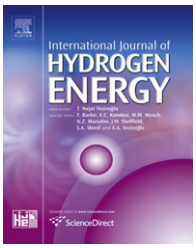

Enhanced photoelectrochemical properties of WO_3 thin films fabricated by reactive magnetron sputtering

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ABSTRACT

Polycrystalline WO_3 thin films were fabricated by reactive magnetron sputtering at a substrate temperature of 350 °C under different Ar/O_2 gas pressures. In order to study the thickness dependence of photoelectrochemical (PEC) behavior of WO_3, the thickness-gradient films were fabricated and patterned using a micro-machined Si-shadow mask during the deposition process. The variation of the sputter pressure leads to the evolution of different microstructures of the thin films. The films fabricated at 2 mTorr sputter pressure are dense and show diminished PEC properties, while the films fabricated at 20 mTorr and 30 mTorr are less dense and exhibit enhanced water photooxidation efficiency. The enhanced photooxidation is attributed to the coexistence of porous microstructure and space charge region enabling improved charge carrier transfer to the electrolyte and back contact. A steady-state photocurrent as high as 2.5 mA cm^{-2} at 1 V vs. an Ag/AgCl (3 M KCl) reference electrode was observed. For WO_3 films fabricated at 20 mTorr and 30 mTorr, the photocurrent increases continuously up to a thickness of 600 nm.

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1. Introduction

The splitting of water into hydrogen and oxygen using solar irradiation is an attractive approach to secure the future supply of clean and sustainable energy [1–5]. In the solar radiation-driven water-splitting reaction the energy of sunlight is directly captured, converted, and stored in the high-energy chemical bonds of hydrogen molecules. Among various strategies to split water, the use of semiconductor-based photoelectrochemical (PEC) cells allowing for spatially separated production of hydrogen and oxygen has attracted significant interest [6–8]. However, the success of this approach depends utterly on our ability to design and fabricate cheap, highly photoactive, and chemically stable semiconducting photoelectrodes. A particular challenge is in the development of highly stable photoanodes for water photooxidation since the rate-determining step in solar water splitting is the oxidation of water to oxygen, which is

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a complex process requiring proton-coupled transfers of four electrons equivalent [9,10]. During the last 30–40 years, three metal oxide n-type semiconductors; TiO_2, Fe_2O_3, and WO_3 have been most extensively studied as potential candidates for photoanode materials in PEC cells [8,11–23]. This is primarily due to their good stability in harsh environments (aqueous electrolyte under continuous solar radiation) and their relative abundance in nature. Taking into account solely their bandgap energy and assuming maximum external quantum efficiencies, the theoretical solar-to-hydrogen (STH) efficiency under solar Air Mass 1.5 Global illumination has been calculated to be the highest for α-Fe_2O_3 (STH efficiency 15%, bandgap 2–2.2 eV), as compared to monoclinic WO_3 (6%, 2.5–2.9 eV), and anatase TiO_2 (1%, 3.2 eV) [24]. However, while having the lowest bandgap, α-Fe_2O_3 electrodes typically suffer from a very positive photocurrent onset potential (ca. 0.8 V vs. the reversible hydrogen electrode, RHE), which requires the application of additional electric bias in water-splitting cells [20]. In the case of WO_3 the photocurrent onset potential is much less positive, ca. 0.4 V vs. RHE [20]. This, together with the possibility to decrease the optical absorption edge of WO_3 by doping, makes WO_3 a highly promising material for PEC cells.

The PEC performance of WO_3 photoanodes depends heavily on their microstructural, optical, and surface properties [13,18,20,25–29]. Accordingly, the search for materials with higher PEC activity inevitably involves fabrication and characterization of a large number of samples. Progress can be accelerated by employing combinatorial material science approaches making use of high-throughput experimentation [30–33]. In our research we employ a combinatorial materials processing approach and high-throughput screening using micro-electromechanical systems (MEMS) tools [34,35]. These represent unique and versatile techniques to study the process parameters–microstructure–functionality relationships for thin film materials. For instance, at fixed process parameters, the thickness-dependent properties of thin film materials can be studied on a materials library fabricated in one experiment, which substantially reduces the number of experiments and therefore saves time and resources, while also reducing the sample-to-sample variability inherent in multiple depositions.

This report focuses on the photocurrent characteristics of WO_3 thin films fabricated by reactive magnetron sputtering as a function of their thickness and microstructural variations. The key processing parameters influencing the thin film micro-morphology that exert a decisive influence on their PEC properties are identified and discussed.

2. Experimental methods

WO_3 thin films were fabricated by reactive magnetron sputtering from a metallic tungsten target (99.99% purity) in a sputter system (AJA International). To suppress arcing during reactive sputtering, units for pulsed direct current (DC) (35 kHz, duty cycle ~95.8%) and an arc suppression unit (Advanced Energy Pinnacle) are connected between the power supply and the tungsten target. The base pressure was below 3.7×10^{-7} Torr. The tungsten target was inclined at an angle of 47° with respect to the substrate normal. The substrates used were prepared separately; 100 nm Pt was coated by radio frequency magnetron sputtering on thermally oxidized Si wafers (1.5 μm SiO_2). The films were deposited in a reactive (Ar/O_2 gas mixture) environment. The sputter pressure was varied between 2 mTorr and 30 mTorr, while the Ar/O_2 ratio was kept 1:3 for all films examined in this work. The substrate was heated up to 350 °C and was kept stationary in order to produce wedge-type WO_3 films with thickness gradient as depicted in Fig. 1. A micro-machined Si-shadow mask was utilized for patterning the WO_3 film on the substrate-stripe (10 mm × 100 mm). The deposition time was adjusted in such a way to deposit around 600 nm thickness of the film at the end (Position 9) closer to the target. The deposition parameters are summarized in Table 1. The fabricated thickness-gradient sample consists of 9 squares (6 mm × 6 mm) separated by 3 mm from adjacent squares. The squares are numbered sequentially from 1 to 9.

The thickness of the fabricated films was determined by a mechanical profilometer (Ambios) measuring the step between the Pt surface and WO_3 film surface created by depositing through openings of the Si-shadow mask. Structural characterization of the samples was carried out by wide-angle X-ray diffraction (XRD) technique using X'Pert PRO X-ray diffractometer (PANalytical; Bragg–Brentano geometry; Nickel-filtered Cu-K_α radiation). The XRD patterns of the samples were recorded in the symmetrically coupled $\omega - 2\theta$ scan mode where 2θ is the diffraction angle and $\omega = \theta$ is the angle of incidence of X-ray radiation. The observed XRD reflection positions were compared with reported reflection positions of tungsten oxides in the powder diffraction data bank [36]. The surface morphology of the films was investigated by a scanning electron microscope (SEM). Transmissions electron microscopy (TEM) investigations were performed using a FEI Tecnai F20 G^2 TEM operating at an acceleration voltage of 200 kV either in bright

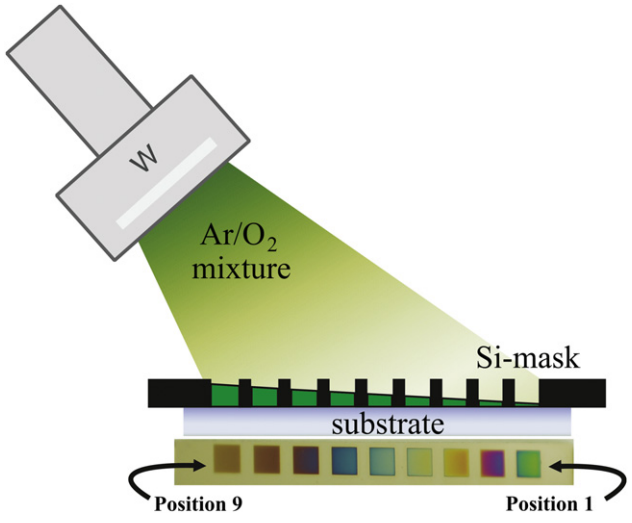

Fig. 1 – Schematic of the fabrication of thickness-gradient WO_3 thin film materials library by reactive sputter deposition. A typical photograph of WO_3 thickness-gradient thin film materials library patterned using a micro-machined Si-mask is shown. The positions 1 and 9 correspond to the thinnest and the thickest films in the materials library, respectively.

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