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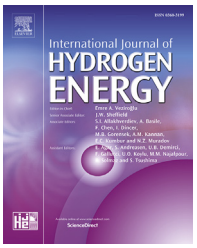

Enhancement in the solar light harvesting ability of tungsten oxide thin films by annealing in vacuum and hydrogen

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ABSTRACT

Thin films of tungsten oxide were fabricated by RF-sputtering. The films were annealed in vacuum and hydrogen at different temperatures to enhance the solar light absorption in the visible and near infrared regions by creating oxygen vacancies and localized surface plasmon resonance. The effect of vacuum and hydrogen annealing on structural, morphology, chemical, electrical and optical properties were investigated. Vacuum-annealed and hydrogen-annealed films behaved like degenerate semiconductor and showed strong absorption in the near-infrared region due to localized surface plasmon resonance. The solar light harvesting properties of as-deposited, vacuum-annealed and hydrogen-annealed tungsten oxide films were examined by measuring their photocurrent response.

Introduction

Metal oxide photocatalysis has attracted significant attention due to its promising application in solar energy conversion since the discovery of water photolysis on a titanium oxide (TiO_2) in the 1970s [1]. TiO_2 is the initial metal oxide photocatalyst investigated for water splitting and nowadays it is still most studied one due to its own advantages [1,2]. TiO_2 is a wide bandgap semiconductor and it is only absorbed ultraviolet light, which greatly limits its practical applications [1,3]. According to energy distribution in the solar spectrum, 54.3% of sunlight at earth surface is located in near infrared region (NIR) (760–3000 nm), 38.9% is located in the visible region (400–760 nm) and 6.8% is located in the ultraviolet region [4]. In addition to extensive research on reducing the band gap of TiO_2 for the visible light response, alternative semiconductors with intrinsic narrow band gaps are being explored [3,4].

Tungsten trioxide, known as a nontoxic and photostable n-type semiconductor with a band gap of ($E_g = 2.6–3.2$ eV) [5]. In WO_3, the conduction band is formed by 5d orbital of tungsten and the valence band is formed by 2p orbital of oxygen [6,7]. In

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pure form of WO_3, the conduction band is empty and act as an insulator. When the WO_3 films are annealed in vacuum, oxygen vacancies (WO_{3-x}) defects states are created near the conduction band. Each oxygen vacancy leaves two electrons behind which is responsible for the decrease in resistivity of tungsten oxide [7]. Tungsten oxide absorbs a significant part of the visible light and, therefore, becomes a compelling photocatalyst for solar light harvesting. Therefore, in the past decades, persistent efforts have been made to improve the photocatalytic activity of WO_3, especially in water oxidation, different strategies have been proposed [5–7].

The photocatalytic activity of any metal oxide can be improved by nanostructuring and by improving its solar light harvesting ability [8–10]. Nanostructuring is a promising strategy to improve the photocatalytic efficiency because nanostructures possess more surface area [10,11]. It was reported that nanocrystalline thin films, mesoporous thin films, and hierarchical hollow shells of semiconductor show better photocatalytic activity than bulk semiconductor material [11–13]. Mohamed *et al.* [14] synthesized nanoporous and nanoflask WO_3 and measured the photocurrent density to evaluate the photocatalytic ability of samples. It was noticed that nanoporous and nanoflask show high photocurrent density because of nanostructuring of WO_3 material [14].

The solar light harvesting ability of metal oxides can be enhanced by introducing oxygen vacancies or by decorating them with metallic nanostructures like gold and silver [15,16]. The introduction of oxygen vacancies states within the band gap of metal oxides enhances their absorption properties, results in better photocatalytic activity [15,17]. Yan *et al.* [18] prepared the tungsten oxide single crystal nanosheets and then annealed them in vacuum and hydrogen. It was observed that vacuum and hydrogen annealed nanosheets showed better photocatalytic activity because strong absorption in the visible and near infrared regions [18]. Yu *et al.* [19] synthesized self-doped WO_{3-x} nanoflask arrays. It was observed that the absorption of self-doped WO_{3-x} was high in the UV and in the visible regions as compared to pure WO_3 samples because of the creation of defects within the band gap. The photocurrent of self-doped WO_{3-x} samples was much higher than pure WO_3 [19].

In the past decade, the solar light harvesting ability of metal oxide was enhanced by decorating them with metallic nanostructures especially gold and silver [16,20]. Gold and silver nanostructures possess LSPR and when it combined with semiconductors, it provides a unique path to harvest the solar light [20]. Yang *et al.* [21] fabricated the silver nanoparticles-decorated N–TiO_2 photoanode for the production of hydrogen under solar light. Under the solar light, electrons are excited in Ag nanoparticles due to LSPR and were transferred to the N–TiO_2 conduction band. This result an increase in the light harvesting ability of N–TiO_2 [21].

Recently, transition-metal oxides are recognized as interesting candidates for LSPR hosts, originated from their outerd valence electrons [18,22,23]. Plasmonic molybdenum oxide nanosheets were synthesized and such plasmonic semiconductor nanostructures exhibited enhanced photocatalytic activity under visible light [22]. Tungsten oxides nanocrystals with tunable LSPR have also been successfully prepared [18,23].

Despite the current achievements, on the strategies to enhance the photocatalytic activity, WO_3-based metal oxides with adequate under solar light is still being explored. Inspired by the pioneer work on WO_3, herein, we fabricated the WO_3 thin films and then annealed them in vacuum and hydrogen for the introduction of abundant oxygen vacancies and the creation of LSPR to promote the light harvesting performance of WO_3.

Experimental details

Tungsten oxide thin films were deposited at 400 °C on fused silica substrates using radio-frequency (RF) magnetron sputtering. The deposition of tungsten oxide films was carried out in an Oerlikon Univex 350 sputtering unit. The sputtering target (WO_3) possessed a purity of 99.99%. When a base pressure 8×10^{-6} mbar was reached, Ar gas was admitted into the chamber at a flow rate of 12 sccm, corresponding to a chamber pressure of 2×10^{-2} mbar. A plasma was generated by applying an RF power of 120 W. The sputtering was carried out for 1 h.

The thickness of the deposited films was determined optically from the maxima and minima of the transmittance spectra. The estimated thickness of the deposited films was 300 ± 10 nm. One set of films was annealed in vacuum at 300 °C, 400 °C and 500 °C named as, V3, V4, and V5 respectively. The pressure during vacuum annealing was 8×10^{-5} mbar. Another set was annealed at 300 °C, 400 °C and 500 °C in a hydrogen environment under a flow rate of 25 sccm named as, H3, H4, and H5 respectively. During hydrogen annealing, the pressure of furnace was 1.89×10^{-1} mbar. The structural properties were studied by x-ray diffraction using a Rigaku Ultima IV diffractometer with Cu $K\alpha$ radiation. The surface morphology of the films was examined using atomic force microscope (Veeco Innova diSPM). The surface of the films was probed with 10 nm radius silicon tip that oscillated at its resonant frequency of 300 kHz. X-ray photoelectron spectroscopy (XPS) performed in a Thermo Scientific Escalab 250Xi spectrometer investigated the chemical properties of the films. The electrical properties were measured using van der pauw Hall effect measurement system (Ecopia HMS 3000). The absorption of the films was studied using spectrophotometer (Jasco V-570). The photocurrent response was measured using a three-electrode electrochemical cell with calomel electrodes as a reference electrode, platinum wire as a counter electrode and films of tungsten oxide act like working electrode. In this experiment, Na_2SO_4 (PH = 7) used as the electrolyte. Metrohm autolab (B.V) Potentiostat/Galvanostat PGSTAT302N used to investigate the photocurrent at a scan rate of 0.5 V/s. The PEC cell was exposed to chopped light (on/off) through oriel sol 3A class AAA solar simulator-Newport (100 mW/cm^2) as a source of illumination. All photoelectrochemical analysis explained according to the normal hydrogen electrode (NHE).

Structural and morphological analysis

Fig. 1 represents the XRD patterns of the as-deposited, vacuum-annealed and hydrogen-annealed films. Identification of