Applied Surface Science 297 (2014) 116–124

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# A comparative study of microstructures on the photoelectric properties of tungsten trioxide films with plate-like arrays

Chaoqun Yang, Qiang Zhu, Shunping Zhang, Zhijun Zou, Kuan Tian, Changsheng Xie *

*State Key Laboratory of Material Processing and Die & Mold Technology, Nanomaterials and Smart Sensors Research Laboratory, Department of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China*

ARTICLE INFO

*Article history:*
Received 10 December 2013
Received in revised form 14 January 2014
Accepted 15 January 2014
Available online 25 January 2014

*Keywords:*
$WO_3$
Photoconductivity
Electron trapping
Infrared light response

ABSTRACT

$WO_3$ plate-like array film was grown on the FTO electrodes by a simple hydrothermal method. In order to change the microstructures of the $WO_3$ films, the as-grown films were further post-heat treated in air and in $H_2$, respectively. The photoresponse characteristics of the as-prepared $WO_3$ films are investigated in the gas phase, and to explain the slow decay of the photocurrent of $WO_3$, the electron trapping effect is proposed. We found that both of the phase structures and oxygen vacancies had great influences on the photoresponse characteristics of $WO_3$ films. For the three $WO_3$ films, the photocurrent decreased significantly with the distortion of the octahedra which were the building blocks of the various crystal structures and with the decreasing of oxygen vacancy concentration. The untreated-$WO_3$ shows 2.5 times higher photocurrent intensity than hydrogen-treated $WO_3$ and the hydrogen-treated $WO_3$ shows 17 times higher photocurrent intensity than air-treated $WO_3$. The experimental results revealed the influence of phase structure on the photoelectric performance of $WO_3$ was far greater than that of oxygen vacancy. We also found that the hydrogen-treated $WO_3$ exhibited excellent infrared photoresponse property, which was 20 times higher than that of the pristine $WO_3$. This was attributed to the existing large number of oxygen vacancies yielding extended energy states which often formed a continuum extending to and overlapping with the conduction band (CB) edge.



## 1. Introduction

$WO_3$ is an indirect band gap (2.4–2.8 eV) semiconductor material which can absorb visible light within the solar spectrum [1,2]. As a type of transition metal oxide, $WO_3$ has attracted great interest because of its distinctive optical [3–6], electrical [7,8], structural [9], and defect properties [10]. It is a kind of promising material for many optoelectronic devices, such as electrochromic devices [11], gas sensors [12,13], information displays [14], etc.

For thin films of $WO_3$, much work has been published on material preparation and performance characterization as well as theoretical understanding. In the literature [15–19], various tungsten oxide ($WO_3$) nanostructures such as nanowires, nanorods, nanotubes, nanosheets, nanowalls and nanoplatelets have already been prepared. A variety of techniques which are used to prepare $WO_3$ films have also been developed [20–26]. Solarska et al. and Amano et al. achieved substantial improvement in enhancing the incident photon-to-current efficiency (IPCE) by morphology modification and impurity doping [27,28]. Penza et al. studied the $NO_x$ gas sensing characteristics of $WO_3$ thin films activated by noble metals (Pd, Pt, Au) layers and reported that the activator layers had an promotional effect on the speed of response to $NO_x$ at low temperature and on selectivity enhanced with respect to other reducing gases (CO, $CH_4$, $H_2$, $SO_2$, $H_2S$, $NH_3$) [29]. Yagia et al. [30] reported that the $WO_3$ films sintered at 550 °C produced 3.7 mA $cm^{-2}$ of a photoanodic current at 1.2 V vs. SCE. Huo and his co-workers investigated the ultraviolet (UV) photoresponse characteristic of the devices containing $WO_3$ films and found that hexagonal-$WO_3$ nanowires exhibited very excellent UV photoresponse property [6]. Via facile hydrogen treatment, Wang et al. enhanced the photostability and photoactivity for water oxidation [1] and Cheng et al. improved the energy conversion efficiency of the DSCs of $WO_3$ [31]. Li and her co-workers found that the hydrogen-treated $WO_3$ has full-spectrum absorption effect and long persistent energy storage ability [32]. Although a lot of work has been carried out based on $WO_3$ films, there are only few reports concerning photoconductivity properties of $WO_3$ thin films over a wide time range. To the best of our knowledge, the reports about the photoelectric response of $WO_3$ films in gas circumstance are fewer.

The aims of this work are to prepare $WO_3$ thin films with different microstructures by post-heat treatment, test the photoelectric property of $WO_3$ films in gas phase circumstance and discuss

* Corresponding author. Tel.: +86 27 87556544; fax: +86 27 87559836.
*E-mail address:* csxie@mail.hust.edu.cn (C. Xie).

0169-4332/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2014.01.095

the differences of $WO_3$ thin films with different microstructures, to comprehend the interaction between light and electrons in semiconductors. In our work, we try to expound the influence of microstructure on the photoelectric property of $WO_3$ films. This will lay the foundation for developing the photosensitive materials for selection and application in the future.

## 2. Experimental details

### 2.1. Material preparing

The analytical grade precursor chemicals used were sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$, 99% Aldrich), tungsten hexachloride ($WCl_6$, 99.6% Alfa Aesar Co., American), ammonia ($NH_3{\cdot}H_2O$, 25–28% soda plant Wuhan), Ammonium oxalate ($(NH_4)_2C_2O_4$, 99.5% Sinopharm) 3 M hydrochloric acid (HCl, Sinopharm), absolute ethanol ($C_2H_5OH$, Sinopharm), and deionized (DI) water. All chemicals were used without further purification. The Fluorine doped Tin oxide (FTO) glass (Nippon Sheet Glass Company in Japan, 2.2 mm of thickness and 20 mm × 20 mm of area, 12 Ω/cm$^2$ of the sheet resistance) was used as substrate.

Before growing the nanoplates, the $WO_3$ seed layers were deposited on the FTO electrodes by the sol–gel method. Beforehand, the FTO films were ablated by using a focused laser beam and were ultrasonically cleaned with acetone, isopropanol, ethanol, and deionized water in sequence. Then, the $WO_3$ sol was prepared. 3.9684 g $WCl_6$ was dissolved into 100 ml DI under intense stir at ~50 °C in water bath. After stirring for 30 min, 0.1 ml 50% $NH_3{\cdot}H_2O$ was added in the above solution. After stirring for 30 min, the solution was aged for 2 days at room temperature (25 °C). The dip coating method was used to coat the sol on the FTO electrodes which had been cleaned and dried. The dip coater (ZR-4200) is made by Zhongrui Instrument Co, Ltd, China. The drawing rate was 100 mm/min and repeated three times, during each process the coated substrates were dried at 80 °C in air for 15 min. Every sample was coated three times. All the substrates were then heated to 400 °C in air for 90 min. The $WO_3$ nanoplate film was grown by hydrothermal method. The growth-promoting media which we used to prepare $WO_3$ films was synthetized according to the method proposed by Yang and his co-workers [22]. Firstly, 0.693 g $Na_2WO_4{\cdot}2H_2O$ was dissolved in 90 ml deionized water, followed by the addition of 30 ml of 3 M HCl. After stirring for 45 min, 0.6 g $(NH_4)_2C_2O_4$ was added into the above solution. The suspension became transparent after several minutes of stirring, then 90 ml deionized water was added into the above solution. A mixed precursor was obtained after magnetic stirring for 30 min. After that, we transferred the solution to autoclaves. The FTO glasses coated with $WO_3$ seed layers were immersed and leaned against the wall of the Teflon-vessel with the conducting side facing up. After the autoclave was sealed, the hydrothermal synthesis was carried out at 160 °C for 2 h. After that, the autoclave was allowed to cool down to room temperature in the oven, then the FTO glasses were taken out and washed with deionized water and methyl alcohol in sequence and finally dried at 80 °C in air for several hours. Then the obtained films were annealed in air and in $H_2$ up to 400 °C at a heating rate of 3 °C/min, and left at 400 °C for 2 h, respectively. Finally they were cooled to room temperature in the furnace, and then the air-treated $WO_3$ and hydrogen-treated $WO_3$ are prepared and denoted as A–$WO_3$ and H–$WO_3$, respectively. The film without annealing is denoted as U–$WO_3$.

### 2.2. Characterizations

XRD analysis was carried out on an X-ray diffractometer (X'Pert PROPANalytical B.V.) using Cu Kα1 radiation in the 2$\theta$ ranges from 20 to 80°. The absorbance of the films was measured with a UV/visible spectrophotometer (Lambda35 PerkinElmer) at room temperature within the wavelength range of 200–100 nm. The surface morphologies were studied using FESEM (Hitachi S-4800 FE-SEM). X-ray photoelectron spectroscopy analyses were performed in a VG ESCA III spectrometer using the Al Kα radiation. The binding energy reference was the C 1s peak at 285.0 eV. The Photoluminescence (PL) spectra were taken in the wavelength range 200–1000 nm by using a Xe lamp as the excitation light source (excitation at 325 nm) at room temperature. The Raman spectra were measured from 50 to 1000 cm$^{-1}$ using a 50 mW and 532 nm wavelength Ar green laser.

### 2.3. Photocurrent measurement

The photoelectric properties of $WO_3$ films were measured by a test platform developed by our laboratory [33,34]. The test platform is mainly composed of, test chamber, light source and signal processing system. The test samples were put into the test chamber, and then the test system started to work. The whole test process was in a dry air stream at room temperature, and the flow of air stream was controlled as 200 mL/min by a mass flow controller. A bias voltage which was 0.1 V had been applied to the electrodes of testing simples. The ultraviolet (UV) (365 nm), blue (465 nm), green (528 nm) and infrared (780 nm) LED array lights (Light Emitting Diode, Shenzhen Ti-Times Co.) were used for illuminating the simples as light sources at 30 s.

The details of the test process were as follows. First, let the dry air continuously flow into the test chamber for 15 min before starting testing in order to eliminate the effect of the humidity or other gas molecules in the test chamber. Then, the bias which we used to separate electron–hole pairs was loaded at 15 s and unloaded at 3000 s. In the testing process, we turn the light on at 30 s for the first time and turn the light off at 300 s, then 600 s on, 900 s off, by analogy, until the end of the fifth cycle.

## 3. Results and discussion

### 3.1. Morphology, optical absorption and structure

$WO_3$ nanoplate films were fabricated on fluorine-doped tin oxide (FTO) substrates, using a seed mediated hydrothermal method. The top-view images in Fig. 1b–d reveal that the surfaces of FTO substrates are covered with $WO_3$ nanoplates. The average length and thickness of the platelets determined from the SEM images are ~500 nm and ~80 nm, respectively. Fig. 1a shows the image of seed layer. We can see that the $WO_3$ seed films prepared by sol–gel dip-coating technique are composed by $WO_3$ nanoparticles. The diameter of $WO_3$ nanoparticles is optically measured ranging between 40 and 50 nm. The cross-sectional image of the film (Fig. 1e) shows the thickness of the $WO_3$ film is about 500 nm.

The EDX spectra of the three kinds of films are shown in Fig. 2. From the spectra, we can see that these samples are of similar composition, mainly containing W and O.

As shown in Fig. 3 (inset), the U–$WO_3$ film is yellow in color. While the A–$WO_3$ film is yellow-white and the H–$WO_3$ film is dark blue. Fig. 3 shows the normalized UV–visible absorption spectra of the as-prepared samples at room temperature. All the samples show fairly identical absorbance in the UV region (<400 nm). However, different samples show different absorption in the visible light region. For the U–$WO_3$, it absorbs most of the UV-blue light, therefore it appears yellow in color. The H–$WO_3$ film shows the highest absorption in orange and red light compared to the U–$WO_3$ film. So it appears dark blue in color. The band gap energies of the three samples are calculated to be 2.32 eV for U–$WO_3$, 2.56 eV for A–$WO_3$ and 2.39 eV for H–$WO_3$ according