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Influence of annealing conditions on anodic tungsten oxide layers and their photoelectrochemical activity

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ABSTRACT

The nanoporous tungsten oxide films having an amorphous structure were prepared in an electrolyte containing fluoride ions via an anodization process. The as-synthesized anodic oxide layers can be easily converted to the monoclinic WO_3 phase upon annealing in air. The as-synthesized and annealed WO_3 layers were investigated by using X-ray diffraction, scanning electron microscopy, and photocurrent spectroscopy. The effect of annealing temperature and annealing time on the oxide morphology, crystal structure and electrochemical properties were studied. The samples were annealed in air at the temperatures ranging from 400 to 600 °C, and it was found that the original porous morphology of oxide is completely lost after annealing at 600 °C. The changes in the average crystallite sizes upon annealing were confirmed by XRD measurements. The photoelectrochemical performance of the annealed WO_3 layers were studied under pulsed UV illumination, and the highest photocurrents were observed at the incident light wavelength of 350 nm for the sample annealed at 500 °C for 2 h. The band gap energy and the positions of conduction and valence band edges were determined for all studied samples.

1. Introduction

Nanostructured transition metal oxides, in particular TiO_2 and WO_3, have recently attracted significant attention in the research community [1,2]. This is due to the unique characteristics of these semiconductors and their potential use in various fields such as solar cells [3,4], photocatalysis [5,6], water splitting [7], sensors [8,9], and electrochromic devices [10].

Nanostructured tungsten oxide possesses very useful properties, e.g., strong photocorrosion stability in aqueous solutions and stable physicochemical properties [11]. The main advantage of this material is its band gap energy (2.6 eV), which is much lower than that of the commonly used titanium dioxide (3.2 eV). In consequence, absorption in the visible light region is significantly increased (up to 12% of the solar spectrum) [12].

Further improvement in the photoelectrochemical performance of semiconducting oxide can be achieved by the use of nanostructured material in order to maximize the surface-to-volume ratio. Among many methods that have been already proposed for the synthesis of nanostructured tungsten oxides, electrochemical anodic oxidation of metallic substrates seems to be very promising strategy as it is simple, inexpensive and effective. A great advantage of nanostructured oxide layers obtained by this method is a relatively good adhesion between the porous film and a conductive metal as well as its perpendicular orientation to the substrate which facilitates an electron transfer path [13]. In addition, similarly to other nanostructured anodic oxides, the morphology of anodic WO_3 depends on anodizing conditions, especially type of the electrolyte and the value of applied potential or current density [14].

As it was already reported [15–17], a suitable heat treatment can strongly affect both the crystallinity and morphology of anodic oxide films. As a result, photoelectrochemical properties of these materials depend on the conditions applied during annealing. Therefore, careful optimization of annealing conditions has a crucial role for the possibility of further application of nanostructured oxide layers. In several papers, the effect of heat treatment on the photoelectrochemical properties of anodic tungsten oxides has been already studied [18–24]. For instance, Caramori et al. have examined the photoelectrochemical activity of anodic WO_3 films obtained in various fluoride ion-containing electrolytes and subjected to annealing at 550 °C for 1 h in air [19]. It was found that such kind of anodic films can offer higher photocurrent densities than the nanocrystalline electrodes prepared by a sol-gel method [19]. On the other hand, Reyes-Gil et al. compared photoelectrochemical behavior of porous WO_3 anodes synthesized at various anodizing

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conditions with compact WO_3 films [21]. It was proved that porosity of the electrode is a key factor responsible for its enhanced photoelectrochemical response. In addition, it was found that the optimal annealing temperature which offers the highest photocurrents generated at the electrode is 400 °C [21]. Similar results were obtained by Chai et al. for anodic WO_3 grown in 0.3 M oxalic acid at 100 V for 30 min [18]. It was demonstrated that increasing annealing temperature above 400 °C leads to a gradual decrease of sample porosity and, in consequence, lower photocurrents are observed [18]. On the contrary, Huang at al. reported that the highest incident photon-to-current efficiency (IPCE) values and the best photoelectrochemical performance were observed for anodic tungsten layers annealed at 450 °C for 3 h [22].

Very recently, Mohamed et al. reported a detailed thermal characterization of anodic porous WO_3 layers formed in the electrolyte containing 0.7 M H_2SO_4 and 6 mM NaF at 40 V for 60 min [20]. The effect of annealing temperature (in the range of 300–500 °C) on the morphology and photoelectrochemical activity of anodic films was studied [20], and the most promising photoelectrochemical properties were observed for the sample annealed at 300 °C. However, the authors focused mainly on the changes in the morphology of top oxide layer, while a detailed inspection of changes in the anodic layer thickness during annealing as well as the evolution of its internal morphology and structure were not performed. These parameters can also have a crucial role in the photoelectrochemical performance of material [23]. Ng et al. have shown that during the thermal annealing in air a compact oxide layer is formed under the anodic oxide film from the tungsten substrate [24]. Moreover, the thickness of this thermally generated oxide film increases significantly with increasing annealing temperature and process duration [24]. As can be seen, some attempts have been made to find the optimal conditions for the thermal treatment of porous anodic tungsten oxide layers. However, as shown above, almost every study was carried out at different conditions, including the annealing time and procedure, as well as the starting morphology of as grown anodic films (they were synthesized under completely different conditions).

Therefore, in this work we present, for the first time, a detailed and systematic study of photoelectrochemical properties of anodic tungsten oxides synthesized by a one-step anodization, in an aqueous solution containing 1 M ammonium sulfate and 0.075 M ammonium fluoride, and then thermally annealed at the temperature range of 400–700 °C. An important part of this investigation was finding possible correlations between annealing conditions, morphology, structure and photoelectrochemical performance of WO_3 layers. It allows to optimize the procedure of synthesis, and finally, to obtain a nanostructured material with the best photoelectrochemical response. For that reason, we decided to optimize not only the temperature applied during the heat treatment but also the duration of this process. The photoelectrochemical characteristics including photocurrent density as a function of wavelength and applied potential, bang gap energies, and positions of conducting and valence bands were investigated for all studied samples.

2. Experimental

Anodic tungsten oxide was synthesized by a single-step anodic oxidation of metallic tungsten (99.95%, 0.2 mm thick GoodFellow) carried out at the constant voltage of 50 V in an aqueous electrolyte containing 1 M ammonium sulfate and 0.075 M ammonium fluoride. Anodization was carried out at 20 °C for 4 h in a two-electrode cell, where the W sample was used as an anode and the Pt plate as a cathode. Afterward, the samples were annealed in air at temperatures ranging from 400 to 700 °C for 2 h with a constant heating rate of 2 °C min^{-1} using a muffle furnace (model FCF 5SHM Z, Czylok). The typical duration of annealing process was 2 h unless stated differently.

The morphological and structural characterizations of anodic WO_3 layers were performed using a field emission scanning electron microscope (FE-SEM/EDS, Hitachi S-4700 with a Noran System 7). The crystallinity and phase composition were determined using the X-ray diffractometer Rigaku Mini Flex II with monochromatic Cu Kα radiation (λ = 1.5418 Å), in the 2θ range of 20°–80° with a step size of 0.5° min^{-1}.

Photoelectrochemical measurements were performed using a three-electrode cell with a quartz window, where nanostructured WO_3 photoanodes were used as a working electrodes (WE), a platinum foil as a counter electrode (CE), and a Luggin capillary with a saturated calomel electrode (SCE) as the reference electrode. The generated photocurrents were measured using a photoelectric spectrometer equipped with the 150 W xenon arc lamp and combined with a potentiostat (Instytut Fotonowy) [15,25–27]. The photoelectrochemical characterization was performed in 0.1 M KNO_3 at the potential range of 0–1 V and wavelengths ranging from 300 to 600 nm.

3. Results and discussion

3.1. Influence of annealing temperature on the morphology and crystallinity of porous anodic WO_3

FE-SEM images of as synthesized anodic tungsten oxide are shown in Fig. 1. As can be seen, as received anodic film exhibits quite irregular porous morphology. The cross sectional image (Fig. 1B) reveals that before heat treatment the anodic oxide layer has a thickness of about 650 nm.

After 2 h of annealing at 400 °C the morphology of anodic WO_3 (Fig. 2A) did not change significantly in comparison with the as-prepared sample. However, a thin compact oxide layer with a thickness of about 100 nm was created underneath the porous

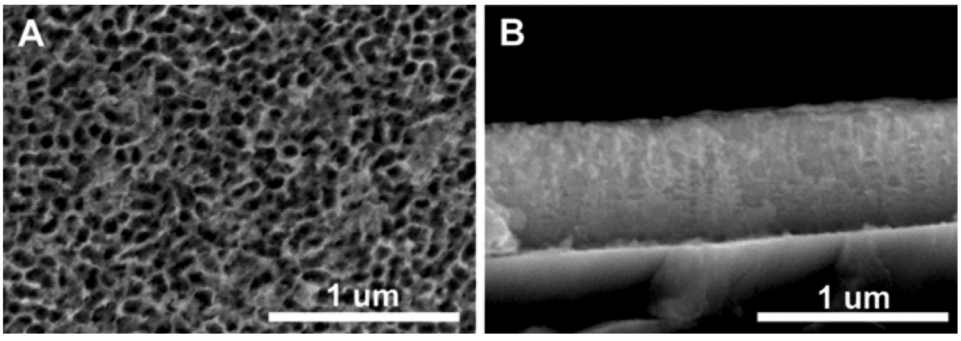

Fig. 1. FE-SEM images of the as-prepared nanostructured tungsten oxide layers: top- (A) and cross-sectional (B) views.