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Efficient plasma-assisted approach in nanostructure fabrication of tungsten

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ABSTRACT

One kind of helium plasma-assisted approach has been presented to fabricate nanostructured tungsten. The morphology and properties evolution of tungsten under helium plasma exposure were investigated as a function of sample temperature, helium ion energy, helium ion dose and helium ion flux. The results show that high crystalline nanostructured tungsten was achieved at 1200 °C. Wavy, meshy and villiform tungsten can be expediently obtained via varying irradiation parameters. Appropriate helium ion energy and ion flux is beneficial to the formation of tungsten with stable nanostructure. The formed nanostructured tungsten was easily oxidized to stoichiometric tungsten trioxide. The as-prepared tungsten trioxide exhibits high light absorption and excellent photoelectrochemical activity. An anodic photocurrent of 3.93 mA/cm^2 was achieved at 1.6 V (vs. Ag/AgCl) under illumination of a 150 W Xe lamp in 0.5 M H_2SO_4 electrolyte.

1. Introduction

Finding adequate solutions for a diversified and sustainable energy supply constitute one of the biggest challenges our society faces today. Enormous efforts have been devoted to discover new methods to exploit the theoretically unlimited sources of renewable energy, such as solar energy, wind energy, and tidal energy. Photoelectrochemical (PEC) water splitting, which captures solar energy and stores it in the chemical bond of H_2 that can be used in many applications, is one of the most promising ways [1–3]. The success of this approach depends utterly on our ability to design and fabricate cheap, highly photoactive, and chemically stable photoelectrodes [4–8].

During the last 30–40 years, n-type semiconductors (e.g. TiO_2, Fe_2O_3 and WO_3) have been extensively studied as potential candidates for photoanodes [9–11]. Among of them, WO_3 is more attractive because of its visible-light response (band gap, Eg = 2.6–2.8 eV), a favorable valance band edge position for O_2 evolution (3 V versus the normal hydrogen electrode, NHE), and exceptional chemical stability in acids and bases [12,13]. To form a high efficiency photoanode, several bottlenecks, such as unfavorable electronic band structure, slow reaction kinetics and mismatch between the absorption depth of visible light and the distance that the photogenerated charge carriers can travel before they recombine, must be eliminated [14]. In general, the first bottleneck can be improved by surface decoration or transition from monoclinic to orthorhombic crystal phase [15,16]. The last two bottlenecks can be overcome via morphology control of photoanode materials. Specifically, geometries with a high BET surface, such as nanowire arrays or hierarchical porous structures, will decrease the distance over which charge transport has to occur and increase the available surface area for reactions [17–19]. In general, the methods used to control morphology can be summarized as wet chemistry methods (e.g. chemical wet etch, anodization, hydrothermal and solvothermal technique) and dry chemistry methods (e.g. spray pyrolysis, thermal evaporation and plasma assisted technique) [20–26].

Although wet chemistry methods can well control the structure of obtained W-based materials, they require prolonged reaction times and highly controlled reaction conditions including temperature, pH value and raw materials ratio [27,28]. In addition, it needs an enormous amount of time to wash the obtained sample and the resulting acid/basic solutions are unfriendly to environment. Dry chemistry methods can overcome aforementioned disadvantages of wet chemistry methods. As one typical dry chemistry method, plasma-assisted approach acts via movement or removal of atom from the surface of object due to the impact of energetic ions. It has been considered as an efficient surface processing technique due to its short-processing time, large yield and low cost. For example, Respinis et al. reported that the time that used to prepare nanostructured tungsten via helium plasma is only about 16.7 min [29]. It also is considered as one promising approach to prepare W-based photoanode. Indeed, as a particular case, the interaction of helium ions with tungsten has been extensively studied because helium ion will be produced in fusion reactors and tungsten is one of the most important plasma facing components in nuclear fusion reactors. However, most researchers focus on improving the stability of tungsten in nuclear fusion reactor. More recently,

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enhancements in the photocatalytic activity have been reported for nanostructured WO_3, made from tungsten via helium ion exposure and following oxidation process [30–32].

To our knowledge, there is rare literature comprehensive investigate the relation of the morphology evolution of tungsten and the process parameter of irradiation. In addition, used as photoanode, tungsten must be oxidized to WO_3. Meanwhile, the morphology effect of tungsten on the stoichiometry of resulting tungsten oxide in the oxidation process is missing. Herein, we chose helium plasma as a typical irradiation system and comprehensively investigate the effects of irradiation parameters, such as temperature, helium ion energy, helium ion dose on the morphology evolution and properties of tungsten in detail. The relation between the morphology of tungsten and stoichiometry of the obtained tungsten oxide was also discussed. The photoelectrochemical activity of the resulting tungsten oxide for splitting water was also studied.

2. Experimental section

2.1. Synthesis of materials

The tungsten dices used in this work was polycrystalline and obtained from Honglu Corporation, China. They were firstly cut into pieces with a dimension of 15 mm × 12 mm × 0.5 mm. These pieces were then mechanically polished to a mirror finish. After polishing, they were rinsed with alcohol and acetone. Finally, these samples were annealed at temperature 1100 °C for 2 h in a vacuum with a background pressure of 10 Pa to relieve internal stresses and reduce the large concentration of nanoscale defects.

Helium ion beam irradiation experiments were performed on large-power material irradiation experiment system (LP-MIES) with various process parameters including sample temperature, ion energy, ion dose and ion flux (see Table 1). Helium ion was perpendicularly bombarded on the sample surface. Finally, a two-step thermal oxidation process was employed to synthesize tungsten oxide. The procedure consists of a short thermal treatment of 2 h at 550 °C followed by further annealing at 400 °C for 4 h (all in flowing O_2).

2.2. Characterization

The crystal structure of the samples were identified by X-ray diffraction (XRD, Rigaku D/MAX III-C) using a diffractometer with Cu Kα radiation (40 kV, 40 mA, λ = 0.15406 nm). Field emission scanning electron microscopy (FE-SEM Hitachi S-4800) was utilized to characterize the obtained samples. A Perkin Elmer Lambda 900 UV/vis/NIR double-beam spectrophotometer with an integrating sphere was used for diffuse reflectance measurements.

2.3. Photoelectrochemical measurement

The photoelectrochemical properties of the obtained tungsten oxide were measured using a typical three-electrode electrochemical PEC cell with a flat quartz window. A platinum foil was used as the counter electrode, and an Ag/AgCl/satd. KCl electrode was used as the reference electrode. The electrochemical measurements were operated in 0.5 M H_2SO_4 by an electrochemical analyzer (Zennium, Zahner, Germany). Simulated sunlight irradiation was obtained with an ABET sun simulator equipped with a 150 W Mercury-Xenon lamp (L2195, Hamamatsu Photonics, Japan). The radiation from the light source was filtered by a visible light (400–700 nm) band pass filter and the irradiated sample area was 0.126 cm^2. The distance between the light guide and the surface of anode was kept at 3 cm [33].

Table 1
Irradiation conditions in the irradiation process.

Sample	Temperature (°C)	Ion energy (eV)	Ion dose (10^{25} ions/m^2)	Ion flux (10^{22} ions/m^2·s)
W-1	800	100	3.1	1
W-2	1000	100	3.1	1
W-2	1200	100	3.1	1
W-4	1500	100	3.1	1
W-5	1725	100	3.1	1
W-6	1200	50	3.1	1
W-7	1200	250	3.1	1
W-8	1200	250	1.0	1
W-9	1200	250	6.2	1
W-10	1200	250	10.0	1
W-11	1200	250	10.0	3

3. Results and discussion

To investigate the effect of temperature on the crystal structure of tungsten, the samples, which were irradiated at different temperature with constant other process parameters, were investigated by XRD (as shown in Fig. 1). From it, one can see that 1200 °C is the turning point. When the sample temperature is lower than it, the diffraction peak intensity will increase with the increase of temperature. However, when the temperature is higher than 1200 °C, it displays opposite trend. In addition, diffraction peak shift of 110 planes is observed. This is because helium ion does not react with tungsten atom. The inserted helium ions will lead to the formation of defects, such as self-interstitials atoms (SIAs) and dislocation loops. These defects will induce a shift of Debye–Scherrer lines towards small angle for an increase of lattice parameters [34]. Meanwhile, SIAs can also be incorporated to dislocation networks. This incorporation behavior will result in crystal lattice expansion and broadening of peaks [35]. These phenomena were also can be observed on the helium irradiated Ti film [36,37]. In addition, these defects are thermodynamically favored in some given temperature ranges. The critical temperature may be 1200 °C in our system used in this work [38]. So, the sample temperature was fixed at 1200 °C.

To investigate the effect of ion energy on the morphology evolution of tungsten, the helium ion dose was fixed as 3.1×10^{25} ions/m^2 and ion energy was set to 50 eV, 100 eV and 250 eV, respectively. As shown in Fig. 2, ripple, wave and hole structures were observed, respectively. This effect may be mainly originated from the interaction between crystal planes and helium ion. As we all know, tungsten has several crystal planes, such as (110), (100), (211) and (101) planes [39]. Among of them, (110) planes is a slip face and its binder energy of tungsten atom to low energy helium ion is higher than other planes [25,40]. Therefore, the pressure inside helium bubbles made from the aggregation of helium ion in this face becomes larger than that in other planes in helium plasma. Consequently, (110) planes may be moved along

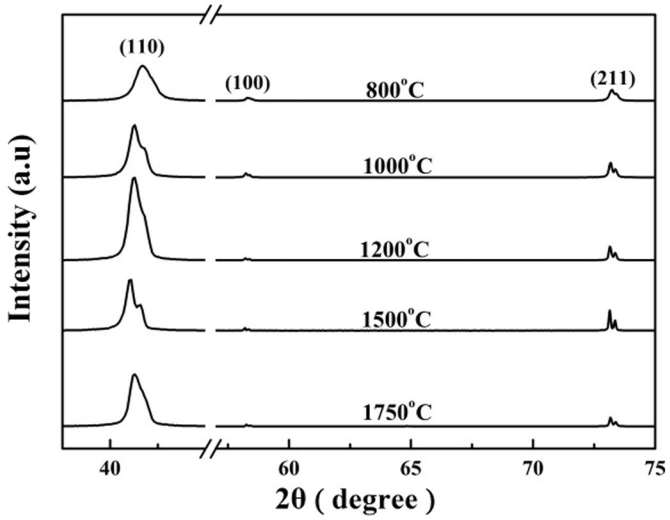

Fig. 1. XRD patterns of tungsten samples irradiated at different temperatures.