Applied Surface Science 447 (2018) 471–478

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Electrochromic behavior of WO_3 thin films prepared by GLAD

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ARTICLE INFO

Article history:
Received 30 October 2017
Revised 26 March 2018
Accepted 31 March 2018
Available online 3 April 2018

Keywords:
GLAD
Annealing treatment
Electrochromic property
Tunable angular selectivity

ABSTRACT

WO_3 thin films fabricated by glancing angle deposition (GLAD) are proposed as excellent electrochromic coatings with favorable ion diffusion. A ~ 500-nm film prepared by GLAD had a relatively large transmittance modulation. The crystallization structure, surface morphology, chemical state, optical and electrochromic properties of WO_3 thin films were systematically characterized upon annealing treatment. Compared with annealed WO_3 porous nanostructured films, the amorphous as-deposited films exhibited a high coloration efficiency and stable reversibility. Furthermore, the GLAD WO_3 films exhibit the tunable angular selectivity under illumination with p-polarized light because of the birefringence, which could extend the application range of nanostructured films in the electrochromic field.

1. Introduction

Electrochromism is a phenomenon whereby the color of some transition-metal oxide materials can be changed reversibly by applying an electric field. Tungsten trioxide (WO_3) electrochromic materials have excellent optical modulation and cycle stability with good application prospects in energy conservation and artificial intelligence, such as smart windows, displays, anti-dazzle mirrors, and effective disguises [1–4]. Based on the electrochemical double injection/extraction of M^+ ions (small size cations, such as H^+, Li^+, Na^+, and K^+) and electrons, amorphous and crystalline WO_3 can be switched reversibly between the colored and bleached states by alternately applying a weak negative and positive voltage [5]. In comparison, nanostructured WO_3 films exhibit a larger surface area for ion diffusion and electron injection/extraction, along with a larger optical contrast ratio, faster switching speed, and higher coloration efficiency [6,7]. Many researchers have investigated the electrochromic properties of nanostructured WO_3 thin films.

Glancing angle deposition (GLAD), which involves manipulating the deposition angle and substrate rotation during the physical vapor deposition process, is a versatile nanofabrication technique based on the self-shadowing effect [8]. Nanostructures prepared by GLAD have the distinctive features of morphology sculpture, hetero-nanostructure design, and composition tenability by manipulating the nanoscale morphology and porosity, which also affect the film birefringence and dichroism [9,10]. Recently, considerable research has focused on nanostructured WO_3 electrochromic films fabricated by GLAD, and improvements in electrochromic performances have been discussed [11–15]. Beydaghyan et al. [14] found that the colored state of GLAD films exhibited an absorption- based coloration in the lower wavelengths as well as an increased reflection in the infrared region. Xiao et al. [12] successfully fabricated highly porous, oriented WO_3 nanocolumns on a flexible substrate by a facile electron-beam evaporation combined with the GLAD technique. Additionally, the electrochromic properties of WO_3 thin films have been studied under different annealing conditions [16–20]. Ng et al. [16] reported that WO_3 nanoplates annealed at 200 °C exhibited a high coloration efficiency, large optical modulation, and good electrochromic cycling stability, as well as short ions insertion and extraction cycles. Sallard et al. [17] demonstrated that sufficient crystallinity of WO_3 films was needed to ensure the cycling stability under realistic environmental conditions. Nevertheless, for nanostructured WO_3 films prepared by GLAD, the influence of annealing on the electrochromic properties are not well-explored. Our previous studies show that annealing treatment causes surface morphology degradation on GLAD films [21–23]. Therefore, the evolutions of the morphological, structural, and optical performances of WO_3 GLAD films under different annealing treatment should be investigated as well. Particularly, the electrochromic property

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https://doi.org/10.1016/j.apsusc.2018.03.248
0169-4332/

of WO_3 GLAD thin films combining with the birefringence is worth pursuing further.

In this study, we present detailed research on WO_3-based thin films fabricated by GLAD. Firstly, the relatively optimal film thickness has been selected by comparing the film optical modulation. Then, morphologies, structures and optical properties are characterized. And the impacts of annealing temperatures on electrochromic properties of WO_3 nanostructured thin films are systematically investigated. Our results extend the knowledge into the tunable angular selective transmittance of tilted nanorods WO_3 films.

2. Experiments

2.1. Synthesis of nanostructured WO_3 films

Fluorine-doped tin oxide (FTO) glass substrates were ultrasonically cleaned in acetone and ethanol for 30 min. WO_3 films were deposited in an electron-beam evaporation chamber with GLAD manipulator [24]. The base pressure was $<1.5 \times 10^{-5}$ Torr, and the distance from the center of the substrates to the WO_3 (purity 99.9%) source material was maintained at 27 cm. With a flow rate of 200 sccm, WO_3 thin films were deposited in a 2-mTorr oxygen atmosphere. The deposition angle between the incident flux and the normal of substrate was set as 70° without rotation and heating. During the coating process, the deposition rate was maintained at approximately 0.25 nm/s via quartz crystal oscillator monitoring. Then, 900-, 500-, and 270-nm films were fabricated. The films were annealed at different temperatures (100, 200, 300, 350, and 400 °C) in air for 2 h at a heating rate of 100 °C·h^{-1} to consider the effect of the annealing temperature.

2.2. Characterizations

The morphologies of the WO_3 thin films were characterized by scanning electron microscopy (SEM, Hitachi S-4700). The crystallographic structures of the WO_3 films were characterized by X-ray diffraction (XRD, Empyrean, PANalytical), adopting a Rigaku D/MAX-2550 with Cu Kα (λ = 1.5408 Å). Raman spectra were measured in Renishaw Invia Raman Spectrometer under a 532.14-nm laser. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 (Thermo Scientific) with an Al Kα emission line at 1486.6 eV and an analyzer pass energy of 10 eV, and the spectra were analyzed using the commercial software Casa XPS. All binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon to correct the shift caused by the charge effect.

2.3. Electrochemical and electrochromic evaluation

The electrochromic performances were obtained using a standard three-electrode, one-compartment electrochemical cell. The WO_3 film (Φ30 mm), a platinum sheet (35 mm × 35 mm), and Ag/AgCl (3.5 mol·L^{-1} KCl) were utilized as the working, counter, and reference electrodes, respectively. The electrolyte solution was hydrochloric acid (1 mol·L^{-1}). By applying voltages between −0.5 V and +0.5 V, chronoamperometry (CA) and cyclic voltammetry (CV) were performed using an electrochemical workstation (UN-O-16027, Zahhner Zennium). The transmittance spectra were measured in the spectral region between 300 and 1000 nm using an ultraviolet (UV)–visible (vis) spectrophotometer (Lambda 900). The p-polarized light transmittance of ±45° symmetry incidence was measured in the spectral region between 300 and 2000 nm.

3. Results and discussion

3.1. Thickness selection

As shown in Fig. 1, the thicker film of 900 nm exhibits a transmittance that is lower than expected because of the higher absorption. We chose films with thicknesses of 500 and 270 nm as subjects to study the transmittance modulation.

As a type of electrochromic material, the WO_3 film is transformed from the bleached state into the colored state by applying a negative voltage, which is represented as $WO_3 + xM^+ + xe^- \leftrightarrow M_x$-$WO_3$ [5], causing crystal structure variation. Then, electrons and cations are expelled out of intracell by applying a positive voltage, and the film changes to a transparent state [25]. Therefore, WO_3 thin films were subjected to a −0.5-V (or +0.5-V) voltage for 10 s to obtain the colored (or bleached) state, and transmittance spectra were measured in the spectral region between 300 and 1000 nm using the spectrophotometer.

As shown in Fig. 2, the transmittance shifts of the 500- and 270-nm films are 42.3% and 29.2% at 633 nm, respectively. However, the 270-nm film is too thin to store more cations and electrons; thus, the colored state of the 270-nm film exhibits a higher transmittance than that of the 500-nm film. Consequently, we shifted our focus to 500 nm as a relatively desirable thickness. According to Fig. 2, for the 500-nm WO_3 film, the transmittance of the colored state decreases with an increasingly negative applied voltage, indicating that a stronger negative voltage yields a larger charge capacity.

3.2. Structural analysis

WO_3 electrochromism is based on the electrochemical double insertion and extraction of electrons and cations, along with the phase transformation. WO_3 film crystallization affects the electrochromic performance as well. Although the structure and morphology of the WO_3 thin film has been considered to be the key roles in determining electrochromic properties [7,26], the influence of the annealing temperature for WO_3 thin films prepared by GLAD is still few reported.

XRD patterns for annealed WO_3 films are shown in Fig. 3. Obviously, no characteristic diffraction peaks of the as-grown sample are observed, which indicates that the as-grown film is in a fully amorphous state. Furthermore, the diffraction peaks of both the 350 °C-annealed sample and the 400 °C-annealed sample are sharp and intense, indicating their highly crystalline nature. No impurity peaks are observed, confirming the high purity of the two samples.

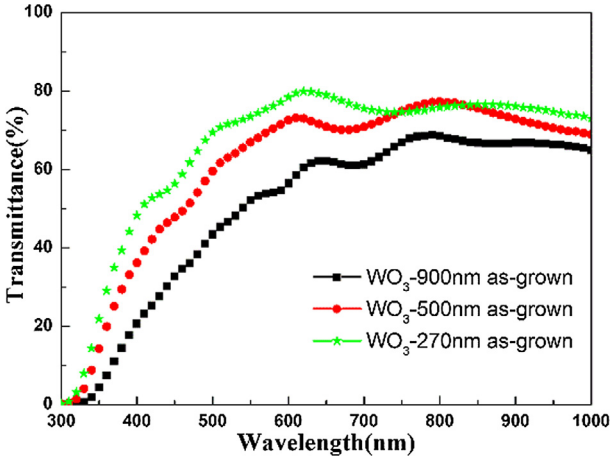

Fig. 1. Transmittance of WO_3 films with thicknesses of 900, 500, and 270 nm.