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Comparison of electrochromic amorphous and crystalline electron beam deposited WO_3 thin films

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Abstract

Tungsten oxide (WO_3) thin films were prepared by an electron beam deposition technique. Films were deposited onto fluorine-doped tin oxide (FTO)-coated glass substrates maintained at 523 K. The as-deposited films were found to be amorphous and crystallized after annealing at 673 K. The electrochromic and optical properties, structure, and morphology are strongly dependent on the annealing conditions. Cyclic voltammetry (C-V) was carried out in the potential range −1 to +1 V. Before and after colouration, the films were characterized by measuring transmittance and reflectance. The colouration efficiencies at 630 nm are about 39.4 $cm^2\ C^{-1}$ and 122.2 $cm^2\ C^{-1}$ for amorphous and crystalline films, respectively. An investigation of self-bleaching for the coloured film revealed that the film fades gradually over time.

Keywords: Tungsten oxide; Thin films; Electrochromic properties; Annealing effect; AFM

1. Introduction

The two major issues facing governments and researchers in Saudi Arabia and Arabian Gulf countries for energy-efficient and comfortable buildings are heating and lighting. Windows provide daylight, but may cause unwanted overheating during the warm season. Since heat transfer through windows is dominated by radiation, optical coatings can be used to improve thermal as well as visual comfort. In a warm climate this can be achieved by using solar control coatings, which decrease the transmittance of the non-visible near infrared radiation from the sun [1]. Today, tungsten oxide is one of the most widely used electrochromic materials, but requires further study, especially under natural conditions outside the laboratory.

Electrochromism refers to the reversible colour change triggered by an applied voltage pulse [1,2]. Electrochromic materials are of interest for displays, rearview mirrors and smart windows [3,4]. Amorphous WO_3 thin films have been prepared by various methods including vacuum evaporation, anodic oxidation, spray pyrolysis, sol–gel, pulsed laser, and sputtering [5–8]. It is well known that the properties of the films are dependent on the preparation conditions. However, further work is required to elucidate the fundamental mechanism of material behaviour to enable the development of new fabrication methods.

In this work, WO_3 was deposited on F-doped SnO_2 (FTO) glass by using an electron beam. The annealing effect was characterized by optical and electrochemical techniques and the film structure was investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM).

2. Experimental technique

Transparent FTO glass substrates, with sheet resistances of about 8 Ω/□, from Solarix Co., were used for the deposition of the WO_3 films. Tungsten trioxide (WO_3) powder with a purity of 99.99% was obtained from Sigma Aldrich

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Co. The evaporation was carried out by electron beam bombardment (Edwards, Auto 306) in a base vacuum of 2×10^{-7} Pa. Amorphous (a-WO_3) films were deposited at a substrate temperature of 523 K. Films annealed in air at 673 K yielded crystallized (c-WO_3) films.

The transmittance, $T(\lambda)$, and reflectance, $R(\lambda)$, spectra of the films were measured at normal incidence and at an incident angle of 5°, respectively. The measurements were acquired in air at room temperature in the spectral range of 190–2500 nm by using a computer-aided double-beam spectrophotometer (Shimadzu 3150 UV–vis–NIR) with a resolution of 0.1 nm.

The electrochemical properties of the films have been characterized by cyclic voltammetry performed on a Pine AFCBP1 Bipotentiostat. Silver chloride was used as a reference electrode and a platinum wire was used as a counter electrode. The liquid electrolyte was 0.1 M H_2SO_4.

The structure of WO_3 was examined using a Shimadzu XRD-6000 X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). The X-ray tube voltage and current were 40 kV and 30 mA, respectively.

The surface microstructure was measured by atomic force microscopy (AFM; Veeco CP-II) in contact mode with Si tips at a scan rate of 1 Hz. The film thickness, deduced from AFM measurements on the edge of the tilted film and also calculated with a film thickness program (Shimadzu UV-2501PC Film Thickness), was estimated to be in the 660–790 nm range.

3. Results and discussion

3.1. Structural properties

Figs. 1a and b show 3D and 2D AFM micrographs of the a-WO_3 film. The 3D figure shows individual columnar grains sticking out from the surface, with a rather small size of about 100 nm, forming a smooth and homogenous surface with an average roughness of about 6.4 nm. However, after annealing at 673 K the small columnar grains merged together to form larger ones with a size of about 150 nm as shown in Fig. 1b. The annealed films are much smoother than the as-deposited films, with a lower surface roughness of about 4.7 nm. Figs. 1c and d are 3D and 2D AFM micrographs of the c-WO_3 film. Figs. 1e and f show the 1 μm × 1 μm surface topology of a-WO_3 and c-WO_3 film, respectively.

Fig. 2 shows the X-ray patterns for FTO glass, as-deposited WO_3 on glass, annealed WO_3 on glass, as-deposited WO_3/FTO (a-WO_3), and annealed WO_3/FTO(c-WO_3). The WO_3/FTO films are amorphous up to a substrate temperature of 523 K. The peaks that appear in the as-deposited film (Fig. 2c) could be attributed to the FTO glass. The crystallization of WO_3 thin films is usually reported to be in the 623–673 K temperature range [5,9]. The presence of a (020) diffraction peak indicates that the long-range atomic order develops gradually above 623 K. The changes are particularly large between 673 and 723 K [10]. This suggests that the crystal structure of WO_3 is sensitive to the deposition or the annealing temperature. Based on tungsten oxide file [JCPDS file 20-1323] and those reported by others [10–15], the XRD pattern of the film in Fig. 2e exhibits polycrystallinity that resembles triclinic WO_3 with a preferred orientation along the (200) direction. The three main peaks are observed at $2\theta = 23.2°$(002), 23.7°(020), 24.5°(200). The intensity of the (200) peak is much higher than that of the same peak obtained on the glass substrate (Fig. 2b), suggesting that the FTO glass substrate enhances the crystallinity of the WO_3 film in the (200) direction.

The average crystal size, D was determined by the Scherrer method [16]

$$D = \frac{S\lambda}{\beta \cos\theta}, \tag{1}$$

where the Scherrer constant, $S = 0.9$, λ is the wavelength of the incident radiation, β is the full width at half maximum intensity, and θ is the Bragg angle corresponding to the peak being considered. The estimated crystal size of the thin film of WO_3/FTO is 44.35 nm for a film annealed at 673 K.

3.2. Electrochemical cycling and electrochromic properties

The electrochromic properties of WO_3 film, i.e. reversible change from colourless in the oxidized state to a deep blue colour in the reduced state, has been extensively studied in the last 30 years. Two different absorption mechanisms are responsible for the colouration of amorphous and crystalline tungsten oxide layers: small polaron transition for amorphous films and Drude-like free electron scattering for crystalline films.

It is generally accepted that amorphous WO_3 film in the bleached state (transparent) can be switched reversibly to a coloured state (dark blue) by insertion of ions and electrons to form tungsten bronze (M_xWO_3) according to the reaction [3,5,17,18]:

$$WO_3\ (\text{transparent}) + xM^+ + xe^- \rightleftharpoons M_xWO_3\ (\text{coloured}), \tag{2}$$

where M^+ is H^+, Li^+, Na^+ or K^+ ions. The inserted electrons reduce some W^{6+} ions to W^{5+} which have $4f^{14}5d^0$ and $4f^{14}5d^1$ configurations, respectively, and polarize their surrounding lattice to form small polarons. The optical response is caused by a small polaron transition between two adjacent nonequivalent sites of tungsten W^{5+} and W^{6+} [17–19] as

$$h\nu + W^{5+}(A) + W^{6+}(B) \rightarrow W^{6+}(A) + W^{5+}(B). \tag{3}$$

On the other hand, the basic colouration mechanism in crystalline tungsten oxide films is attributed to a Drude-like free electron absorption with a behaviour very similar to a heavily doped semiconductors with ionized impurities [20,21]. When ions and electrons are inserted into the crystalline tungsten oxide films, the electrons enter extended