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Electrochromic study on amorphous tungsten oxide films by sputtering

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ABSTRACT

Tungsten oxide films under different oxygen flow rates are deposited by DC sputtering. The voltage change at target and analyses for the deposited films by X-ray diffraction, scanning electronic microscope, X-ray photoelectron spectroscopy and ultraviolet–visible-near infrared spectroscopy consistently indicate that low oxygen flow rate (5 sccm) only creates metal-rich tungsten oxide films, while higher oxygen flow rate (10–20 sccm) assures the deposition of amorphous WO_3 films. To explore the electrochromic function of deposited WO_3 films, we use electrochemical tests to perform the insertion of lithium ions and electrons into films. The WO_3 films switch between color and bleach states effectively by both potentiostat and cyclic voltammetry. Quantitative evaluation on electrochemical tests indicates that WO_3 film with composition close to its stoichiometry is an optimal choice for electrochromic function.

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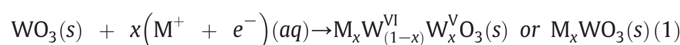
1. Introduction

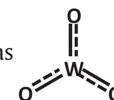
The switch of color in WO_3 thin films between dark blue (colored) and transparent (bleached) states by the insertion of small cations and electrons is known to be electrochromism [1–3]. It is commonly believed that the color change is mainly due to the alteration of valance states from W^{+6} to W^{+5}. Such a transition is made possible by the transfer of electrons from the inserted ion to tungsten atoms and yet maintains the oxide structure. A general reaction of the insertion in aqueous solution can be stated as [3–5]:



$$WO_3(s) + x\left(M^+ + e^-\right)(aq) \rightarrow M_xW^{VI}_{(1-x)}W^{V}_{x}O_3(s) \ or \ M_xWO_3(s) \quad (1)$$

where the cation is represented by M^+, and W^{VI} and W^{V} denote the ions of W^{+6} and W^{+5} respectively.

The sub-stoichiometric valence W^{+5} has higher optical absorption in the range of visible light and thus makes WO_3 films dark blue. There are two characters of the coloration in WO_3. First, it is reversible as long as the transferred electrons are removed to recover the state of W^{+6}. Secondly, the colored state is metastable i.e., it is persistent upon the switch of direction of electrical current. Both characters lend great advantages for applications in electronic devices and display components and optical shielding [4–8].

The most common states of tungsten ions in WO_3 is W^{+6} and W^{+4}. The chemical formula of the former is usually expressed as  and the latter O=W=O. But the actual structure of WO_3 is a monoclinic octahedron with tungsten at the center surrounded by six neighboring oxygen, whereas the WO_2 can be a quadrilateral with central tungsten and four neighboring oxygen. The W^{+4} ions can be viewed as the consequence of incomplete bonding between W and O in the octahedron of W^{+6} [9,10]. Another interesting thought about WO_3 is to resemble its structure as a "B-site empty-perovskite" [11–13] (cf. Fig. 1). If we join octahedrons together, whether by edges or corners, the empty B-site provides space for interstitials like small cations such as Li^+ or H^+ (Fig. 1) and these interstitials are the sources for electrochromism.

Both W^{+6} and W^{+4} do not form polarons, the optical absorption in W^{+6} and W^{+4} are low so the films of pure WO_3 are almost transparent in visible light [14].

A hefty of studies for crystalline WO_3 films can be found in the literature, for instance in [9,13,16], but much less for amorphous WO_3 and its functions. The amorphous films are more transparent and less influenced by the defects but its electrochromic performance remains unclear. A common choice of fabricating tungsten oxide films is by sputtering. However, one particular question in the sputtering process is the control of O_2 flow to generate desirable amount of oxygen ions. The oxygen ions then react with the sputtered tungsten from the target inside the plasma zone to deposit onto a substrate [15–17]. As a result, the structures and the properties of deposited films shall heavily depend on the amount of feed-in O_2. To maintain the amorphous

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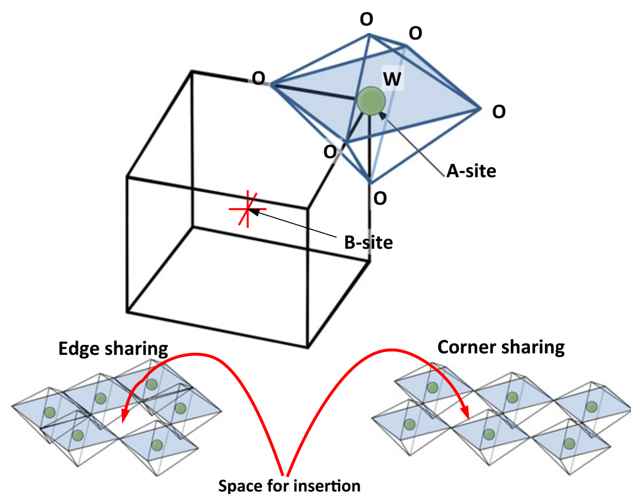

Fig. 1. Microstructures of tungsten oxide.

structures of deposited films, a well-controlled direct-current (DC) sputtering process was prudently carried out in this study [9,10,12,14, 18–21].

To examine, characterize and test the deposited films, the following equipment and experiments were employed: surface profiler for the thicknesses and deposition rates; X-ray diffraction (XRD) and Raman spectrometer for the structures; X-ray photoelectron spectrometer (XPS) for the chemical and elemental analysis; ultraviolet–visible-near infrared (UV–Vis-NIR) spectroscopy for the optical properties; scanning electron microscope (SEM) for the surface morphologies; and electrochemistry for the electrochromic function of deposited films.

2. Experiment

There are two parts in this experimental study. One is the characterizations of films after deposition and the other is the electrochemistry for the electrochromic function of films. Details of experiments will be discussed in the following section.

2.1. Substrate preparation

The working gas during sputtering is pure Ar (99.995%) and O_2 (99.999%) purchased from local suppliers. Substrates are silicon wafer (n-type <100>, $\phi = 4''$, 525 ± 25 μm, Woodruff Tech. USA), Corning glass (Eagle XG®, 100 mm × 100 mm × 0.7 mm) and indium tin oxide glass (ITO, 400 mm × 50 mm × 0.7 mm). Solutions for substrate cleaning are potassium hydroxide (KOH, 1 g/100 ml), acetone (100%), alcohol (95%) and de-ionized (DI) water.

Except the ITO substrate, the cut glass (20 mm × 20 mm × 0.7 mm) was first thoroughly cleaned by KOH solution to remove all containments and organic oils. The substrate was then further cleaned by ultrasound in de-ionized water for 3 min to remove delicate soils. Then the substrate was cleaned several times in acetone DI water and alcohol in turns by ultrasound. After sonication, the substrate was blow-dried using nitrogen ready for sputtering process.

2.2. Film deposition

The physical vapor deposition chamber with the substrate inside was first vacuumed at 6.4×10^{-3} Pa at room temperature. Then Ar was pumped in at 35 sccm and the DC power supply (90 W) was turned on for 4 min. This is mainly to clean up the volatile contaminants on the substrate. After this, O_2 was gradually pumped in until the flow rate reached 20 sccm. The flow rate was step increased at a chosen flow rate (5 or 1.5 sccm) and each increase was kept for 2 min in order to have a stable measurement of the target voltage. The WO_3 thin film started depositing soon after the oxygen was turned on. In the chamber, the distance between the antennae and substrate was about 13 cm. All process parameters are tabulated in Table 1. Note that the working pressure varied from 5.0 to 16 mTorr (0.67–2.13 Pa) according to different O_2 flow rates (0–20 sccm) during deposition. An automatic pressure control (APC) valve is set to regulate the chamber pressure.

2.3. Characterization

2.3.1. Material characterizations

- Structure and elemental composition
  The X-ray diffractometer (XRD, Philips PW3050) using monochromatic high intensity Cu Kα radiation (λ = 1.5425 Å) was used to determine the crystal structures of deposited films. The scanning angle was from 20°–2θ to 65°–2θ, with a step size of 0.04° and measuring time of 1.2 per step. The working voltage is 40 kV and current is 30 mA.
- Surface profile and morphology
  Thicknesses of deposited WO_3 films were evaluated by surface profiler (Surfcordor ET3000, Kosaka). Before measuring, part of the deposited film was first delineated and removed by acetone. The measurement was taken along five randomly selected lines on the sample surface across the edge of the deposited film. The average of these five measured data was counted as the film thickness.
  The morphology of deposited film was imaged by field emission scanning electron microscope (FE-SEM, JEOL, JSM-6701F, Jeol, Ltd., Japan). The voltage of accelerated electron beam is set at 8–10 kV and the magnification is chosen to be 50,000 for the best resolution.
- Raman spectroscopy
  To examine the amorphousness of films, Raman spectrometer (iHR 550, Horiba, Japan) was used to detect the Raman shift of the deposited WO_3 films due to the formation of crystalline Si. The system has a resolution of 0.025 nm and spectral range between 150 and 1500 nm. The excitation wavelength used was a 632.8 nm (25 mW) He–Ne laser. Relevant peaks of Raman shift for tungsten oxides shall be listed later in Section 3 Results and discussion [14,22–30].
- Surface chemical composition
  Surface chemical compositions of films were examined by X-ray photoelectron spectrometer (XPS, Microfocus Monochromatic Al anode X-ray, Thermo Scientific, USA). The irradiated energy by the beam of X-ray caused electrons from 1 to 10 nm underneath the surface to escape, which gave a direct measurement on the binding energy of the emitted electrons following the expression,

$$E_{binding} = h\nu - (E_{K.E.} + \phi) \tag{2}$$

where $E_{binding}$ is the binding energy of electrons, $h\nu$ is the energy of the X-ray, $E_{K.E.}$ is the kinetic energy of the electron, and ϕ is the work function of the spectrometer. The chemical compositions of films can then be determined from the spectrum of the binding energy. During operation, the chamber was vacuumed at 5×10^{-9} Torr (6.67×10^{-7} Pa)

Table 1
Sputtering process parameters for depositing WO_3 thin films.

Process Parameters	
Target power (DC, W)	90
Substrate bias (W)	0
Background pressure (Torr/Pa)	4.8×10^{-6} (0.0064)
Working pressure (mTorr/Pa)	~5.0–~16.0 (~0.67–~2.13)
Substrate temperature (°C)	Room temperature
Target-substrate distance (cm)	~13
O_2 flow rate (sccm)	0–20
Ar flow rate (sccm)	35
WO_3 film thickness (nm)	~197–~202

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