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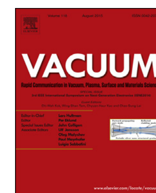

The deposition and microstructure of amorphous tungsten oxide films by sputtering

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A B S T R A C T

Amorphous tungsten oxide film under different oxygen flow rates were deposited by direct current sputtering. The deposition process was monitored by the Langmuir probe and optical emission spectrometer. From the voltage change at target and all plasma parameters, the deposited films under low oxygen flow rate (5 sccm) are metal-rich tungsten oxides. The films were completely oxidized under higher oxygen flow rate (10–20 sccm). The color of films is also changed from dark blue to transparent accordingly. We analyzed the deposited films by XRD, SEM, EDS and XPS confirmed that the compositions change of deposited films. More interestingly, the XPS reveals the existence of inter-valance state W^{5+} in all sample films besides the commonly recognized W^{6+} and W^{4+} states. This may be accredited to the incomplete bonding between tungsten and oxygen due to the amorphous structures of films. The color change of deposited films examined by the UV–Vis–NIR spectroscopy indicates that the optical band gap is widened and absorbance reduced for films deposited under high oxygen flow rate. These results together indicate that WO_3 films with compositions between metal-rich and full oxide are easier for chemical insertion of electrons and ions to achieve better electrochromic functions.

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1. Introduction

WO_3 thin films are known to be electrochromic and capable of switching between colored and transparent (bleached) states upon the insertion of cations such as H^+ or Li^+ [1–3]. This color change is believed due to the transition of electrons between the inserted ions and tungsten atoms, which alters the valance of tungsten from W^{+6} to W^{+5} [4,5]. The sub-stoichiometric valence state W^{+5} has higher optical absorption in the range of visible light and thus appears dark blue. The process of coloration is reversible as long as the transferred electrons are removed to recover the state of W^{+6}. Moreover, the electrochromic change of WO_3 is persistent rather than temporal, i.e., metastable in each of the two states once switched, which is advantageous in applications such as electronic devices for display and optical shielding [6–8].

In addition to W^{+5} and W^{+6} ions, there also exist W^{+4} ions almost ubiquitously in WO_3 due to the incomplete bonding between tungsten and oxygen [9,10]. The structure of WO_3 (W^{+6}) is an octahedron with tungsten at the center and occupies one corner of a unit cell. The oxygen atoms then sit at the edge centers of the unit cell. Under this view, WO_3 is commonly referred as a “B-site empty-perovskite” [11–14]. This empty center provides space for interstitials when WO_3 octahedrons join and stack together by linking their corner oxygen atoms. In contrast, the structure of W^{+4} ions may be thought as a plane with four oxygen atoms bonded to the central tungsten [9,10]. Both W^{+6} and W^{+4} do not form polarons, their optical absorption are low so the films of pure WO_3 are almost transparent in visible light [15].

Studies on the properties of crystalline WO_3 films can be found abundantly in literature. The amorphous WO_3 films attract less attention compared to their crystalline counterparts and in fact most as-deposited WO_3 films by physical vapor deposition are amorphous [16–19]. The amorphousness lacks a long range ordered structure and thus cannot guarantee the space for interstitials, which is crucial in terms of the desired electrochromism of WO_3 films. However, the amorphous structure is also prone to contain a large amount of incomplete bond tungsten and oxygen along with lone pair or half unpaired

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electrons. This means the existence of W^{+4} and W^{+5} ions and more oxygen vacancies, which, in the above discussion, makes the WO_3 films to have higher optical transmittance, higher electrical capacity (charge density) and efficiency in coloration by cyclic voltammetry. These characters also imply longer life time and durable or sustainable in coloration by electrochemical reaction due to the less organized microstructure [20–34]. Another interesting point of the amorphous structure is that its density is lower and diffusion pathways are less organized. The combined effect is faster kinetics for (i) optical absorption in the colored phase; (ii) high coloration efficiency; (iii) fast response both in the process of bleaching and coloration; and (iv) slow bleaching when electrical potential is removed [20,23,25–29,33,34].

In this study, we fabricate the tungsten oxide films by sputtering using mixture of Ar and O_2. Argon is the carrier of plasma while oxygen reacts with sputtered tungsten to deposit on substrates. A key question of this process is the precise control of Ar and O_2 gas flow to obtain amorphous tungsten oxide films [9,11,14,16,19–36]. The correlations among the plasma characteristics, the microstructures and the properties of deposited films were cautiously investigated by Langmuir probe, optical emission spectrometer (OES), surface profiler, scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectrometer, X-ray photoelectron spectrometer (XPS), energy dispersive spectrometer (EDS) and UV–Vis–NIR spectrometer.

2. Experiment

2.1. Substrate preparation

The working gas during physical vapor deposition (PVD) 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) or Corning glass (Eagle XG®, 100 mm × 100 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.

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 then was further cleaned by ultrasound in deionized 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 blown to dry using nitrogen ready for PVD process.

2.2. Film deposition

The PVD chamber with glass substrate inside was first vacuumed to 6.4×10^{-4} Pa at room temperature. Then Ar was pumped in at 30 sccm and the 120 W DC power supply was turned on for 4 min. This is meant to remove the volatile contaminants on the substrate. After this, O_2 was pumped gradually until the flow reached 30 sccm. The flow rate was step increased at 2 sccm and each increase was kept for 2 min in order to have a stable measurement of the target voltage. The deposition of WO_3 thin film started as soon as 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. In this study, O_2 flow rate is the main variable and we like to study their influences on the structures of films. Note that the working pressure varied from ~6.4×10^{-1} to ~2.1 Pa according to different O_2 flow rates during deposition. An automatic pressure control (APC) valve was set to regulate the chamber pressure.

Table 1
PVD process parameters for depositing WO_3 thin films.

Process parameters	
Target power (DC, W)	120
Substrate bias (W)	0
Background pressure (Pa)	6.4×10^{-4}
Working pressure (Pa)	~6.4×10^{-1} to ~2.1
Substrate temperature (°c)	Room temperature
Target-substrate distance (cm)	13
O_2 flow rate (sccm)	0–30
Ar flow rate (sccm)	35
WO_3 film thickness (nm)	~360–380

2.3. Characterization

2.3.1. Plasma characterization

Langmuir probe (Espion, Hiden Analytical, UK) was used to measure the plasma potential, electron and ion density inside the chamber during deposition. The probe was inserted into chamber between the antennae and substrate with its tip positioned around the center of plasma zone. Calibration of voltage and current was carried out before every round of measurement. After calibrations, the range of probe voltage was set up between −30 V and 50 V with resolution of 0.4 V and maximum current around 23.776 mA. The probe was set to scan 3 times, each for about 1.77 s.

For the detection of excited species in plasma, an optical emission spectrometer (OES, Emicon HR system, Plasus, German) was employed. The probe's camera was attached to the chamber window made of quartz. The window was cleaned by organic solution every time before deposition to minimize the optical interference. The spectrum range was set to 195–875 nm of wavelength.

2.3.2. Material characterizations

- Structure

The crystal structure of deposited films was determined by the X-ray diffractometer (XRD, Philips PW3050) using monochromatic high intensity Cu Kα radiation ($\lambda = 1.5425$ Å). 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 was 40 kV and current was 30 mA.

- Thickness and Surface Morphology

Thicknesses of deposited WO_3 films were evaluated by surface profiler (Surfcordor ET3000, Kosaka). Before measuring, part of the deposited film was delineated and removed by acetone at first. The measurement was taken along five randomly selected lines on the sample surface across the edge of deposited film. Average of these five measured data was counted as the film thickness.

The morphology of deposited 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 ensure the amorphousness of films, Raman spectrometer (iHR 550, Horiba, Japan) was used to detect the Raman shift of the deposited WO_3 films. The system has resolution of 0.025 nm and spectral range between 150 and 1500 nm. The excitation wavelength was a 632.8 nm (25 mW) He–Ne laser. Relevant peaks of Raman shift for tungsten oxides can be found in Refs. [37–44] and will be discussed later.

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