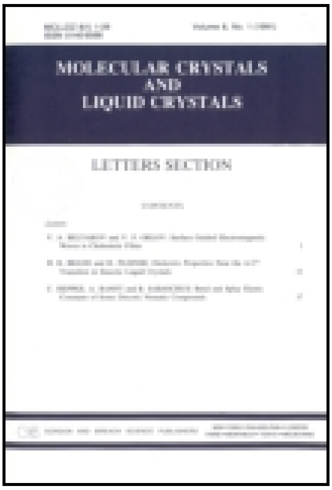

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Min Hong Kim[a], Chung Wung Bark[a], Hyung Wook Choi[a] & Kyung Hwan Kim[a]

[a] Department of Electrical Engineering, Gachon University, Seongnam, Gyeonggi, Korea

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Working Pressure Dependence of $WO_{3\text{-}x}$ Thin Films Prepared by Reactive Facing Targets Sputtering

MIN HONG KIM, CHUNG WUNG BARK,
HYUNG WOOK CHOI, AND KYUNG HWAN KIM*

Department of Electrical Engineering, Gachon University, Seongnam, Gyeonggi, Korea

Tungsten oxide ($WO_{3\text{-}x}$) thin films for an electrochromic (EC) device were deposited at an oxygen flow ratio [O_2/(Ar + O_2)] of 0.7 using reactive facing-target sputtering with a variable working pressure. The correlation between the $WO_{3\text{-}x}$ thin films and EC properties was investigated. The films structural properties were measured by X-ray diffraction; the indium tin oxide diffraction peak was observed in all the films. The electrochemical and optical properties were measured by cyclic voltammetry and UV/Vis spectrometry. The $WO_{3\text{-}x}$ thin film obtained at 0.13 Pa displayed a maximum coloration efficiency of 31.42 cm^2/C, which indicated superior EC properties.

Keywords Tungsten oxide; working pressure; facing-target sputtering; electrochromic; oxygen flow ratio; reactive sputtering

Introduction

Electrochromism is a phenomenon in which the optical properties of a material experience reversible and persistent changes when induced by an external voltage [1]. It has been a subject of extensive studies in both basic and applied research during last few decades. For example, the development of energy-efficient windows exploiting the electrochromic (EC) phenomenon contributes to energy savings; high-performance smart windows are a combination of multiple glass plates, each with its own specific function such as low emission or variable transmittance. The use of EC devices contributes to energy savings in cooling and heating, and offers adjustable lighting levels for user comfort [2]. Electrochromic properties indicates in various transition metal oxides [3]. Among them, tungsten oxide (WO_3) has outstanding EC performance compared to the other transition metal oxides, and has therefore received significant attention from researchers for its application in EC devices [4]. The EC properties of WO_3 thin films are influenced by their microstructure, chemical composition, and synthesis process [5]. WO_3 thin films have been synthesized by various techniques including sputtering, pulsed-laser deposition, sol-gel synthesis, thermal evaporation, electrophoretic deposition (EPD), chemical-vapor deposition, and electron-beam evaporation [6–12]. In this study, we used the facing-target sputtering (FTS) method, which

*Address correspondence to K. H. Kim, Department of Electrical Engineering, Gachon University, Seongnamdearo 1342, Bokjeong, Sujeong, Seongnam; Gyeonggi 461-701, Korea (ROK). E-mail: khkim@gachon.ac.kr

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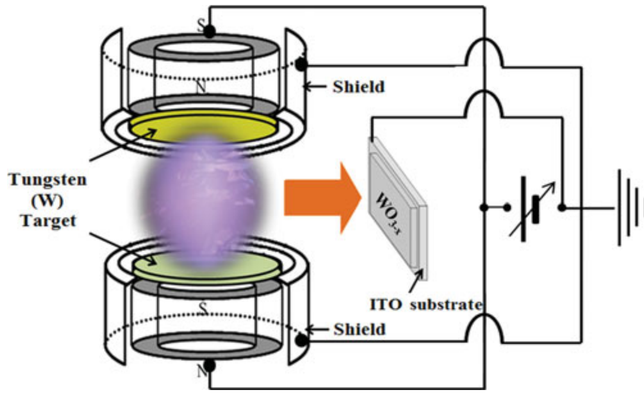

Figure 1. Facing targets sputtering system equipment.

has many advantages such as low damage to films and high plasma density [13]. WO_{3-x} thin films were deposited by FTS in an atmosphere of an argon and oxygen gas mixture under variable working pressure. As the objective of this research is to improve the efficiency of the thin films, the correlation between the tungsten oxide thin films and their EC properties was investigated.

Experimental

Deposition of WO_{3-x} Thin Films

Figure 1 shows the FTS equipment used in the deposition process. A general sputtering system is designed so that the sputter target faces the substrate. The resulting deposition rate is high because the particles of the target are deposited directly on the substrate. However, the properties of the thin films obtained are compromised because of damage from the collision of particles with the substrate. The FTS system is designed such that two targets face each other, and the plasma formed is in a spiral shape. The electrons are confined in the spiral shape, resulting in a high-density plasma. It is well known that this system has many advantages such as low working pressure, low substrate temperature, low damage, and high plasma density, while it also protects the substrate and thin film from the bombardment of high-energy particles, such as electrons and partial ions, during the sputtering process, thus preventing damage [13]. The FTS system is therefore one of the most attractive techniques for the fabrication of high-quality thin films.

Prior to film deposition in our study, glass substrates coated with indium tin oxide (ITO) were ultrasonically cleaned in acetone, distilled water, and ethyl alcohol for 20 min, 10 min, and 20 min, respectively, and then dried under a stream of N_2 gas. The sputtering chamber was evacuated to 2.4×10^{-4} Pa (1.8×10^{-6} torr) using a turbomolecular pump before gases were introduced. The tungsten oxide thin films were deposited onto the ITO-coated glass substrates from a W metal target (99.95% purity, 2 in., LTS Research Laboratories, Inc., USA) at room temperature by reactive FTS in an argon and oxygen plasma. The target was sputtered for 30 min before deposition to remove any oxide layer from the surface. The oxygen flow ratiowas adjusted by mass-flow controllers with a constant $O_2/(Ar + O_2)$ ratio of 0.7, and the resulting total pressure, P, was varied from 0.10 to 1.33 Pa. Table 1 summarizes the sputtering parameters for WO_{3-x} thin-film deposition.

Table 1. Deposition condition of WO_{3-x} thin films

Deposition parameter	Sputtering condition
Target	W (pure 99.95%)
Substrate	ITO coated glass
Power density	4 W/cm^2
Backgroud pressure	2.4×10^{-4} Pa
Working pressure	0.10, 0.13, 0.53, 0.93, 1.33 Pa
O_2 gas flow ratio [O_2/Ar+O_2]	0.7
Thickness	450 nm
Substrate temperature	R.T.

Characterization

The thickness of the WO_{3-x} thin films was measured using a surface profiler (Alpha-Step); the crystal structure of the WO_{3-x} thin films was investigated by X-ray diffraction (D/MAX-2200, Rigaku, Japan); and the optical properties were measured using a UV/Vis spectrometer (Lambda 750, PerkinElmer, USA). The EC properties were measured by cyclic voltammetry (VSP-CHAS potentiostat), which was performed using a three-electrode system consisting of WO_{3-x} as the working electrode, Ag/AgCl (3 M NaCl) as the reference electrode, and a Pt wire as the counter electrode. The electrolyte was a 0.1 M $LiClO_4$–propylene carbonate solution. The scan rate of the measurements was 30 mV/s and the voltage range was −1.5 to 1.5 V.

Results and Discussion

Figure 2 shows X-ray diffraction patterns of the tungsten oxide thin films. The ITO diffraction peak was seen in all the films, and no significant difference in the XRD patterns was

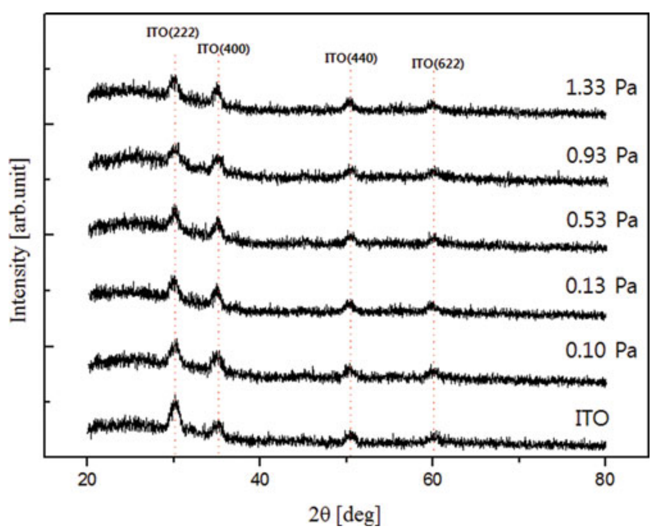

Figure 2. X-ray diffraction patterns of the deposited WO_{3-x} thin films.

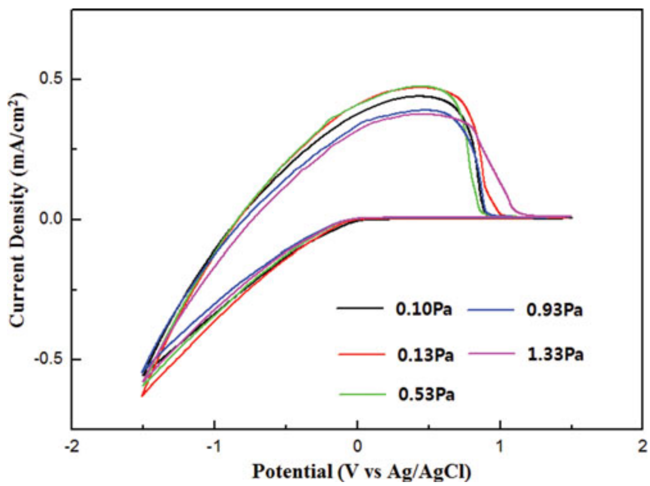

Figure 3. Cyclic voltammograms (CVs) of the deposited WO_{3-x} thin films.

observed. Therefore, the variations in working pressure did not have any significant effect on the films, indicated by a pattern characteristic of their amorphous phase caused by the internal stress in the films [14]. In general, amorphous tungsten oxide thin films exhibit better properties than the crystalline thin films. It is usually a properties of thin films fabricated by sputtering system at room temperature. Figure 3 shows the cyclic voltammograms (CVs) of the WO_{3-x} thin films as a function of the working pressure. The CVs were recorded at a scanning rate of 30 mV/s between −1.5 and 1.5 V to evaluate the EC performance. It is well known that the injection and extraction of electrons and Li^+ ions from the electrolyte result in the coloration and bleaching processes of tungsten oxide thin films, which can be expressed as [15],

$$WO_{3-x}\text{ (bleached)} + xe^- + xLi^+ \leftrightarrow Li_xWO_{3-x}\text{ (colored)},$$

where Li^+ is an ion in the lithium perchlorate organic solution. When a negative bias was applied, the current increased negatively with increasing cathodic potential, corresponding to the co-injection of electrons and Li^+ ions into WO_{3-x} to form tungsten bronzes. The anodic peaks occurred during the positive-bias scan, corresponding to the extraction of electrons and Li+ ions from Li_xWO_{3-x} to the electrolyte. Obviously, the anodic and cathodic peaks exhibited symmetry, and the CV curves showed reversible EC performance of the WO_{3-x} thin films, Regardless of the working pressure, CV curves exhibited a similar form. The high cathodic current density of about 0.64 mA/cm^2 was obtained for the thin film deposited at 0.13 Pa, indicating higher levels of injection and extraction of electrons and Li^+ ions during the CV process. Figure 4 shows the optical transmittance spectra of the WO_{3-x} thin films deposited at 0.10, 0.13, 0.53, 0.93, and 1.33 Pa, which are denoted the as-deposited, colored, and bleached states in the visible range. The values of transmittance for all the deposited WO_{3-x} thin films were approximately 79.42% in the visible range, regardless of the working pressure. Generally, WO_{3-x} thin films have a transparent state if x is below 0.3[16]. The oscillation trends shown in transmittance spectra are related to the thin-film thickness and arise from optical interference from the multilayered components [17]. The color of the WO_{3-x} thin films in our study turned dark blue when electrons and Li^+ ions were electrochemically injected into them. An EC device can change its optical properties

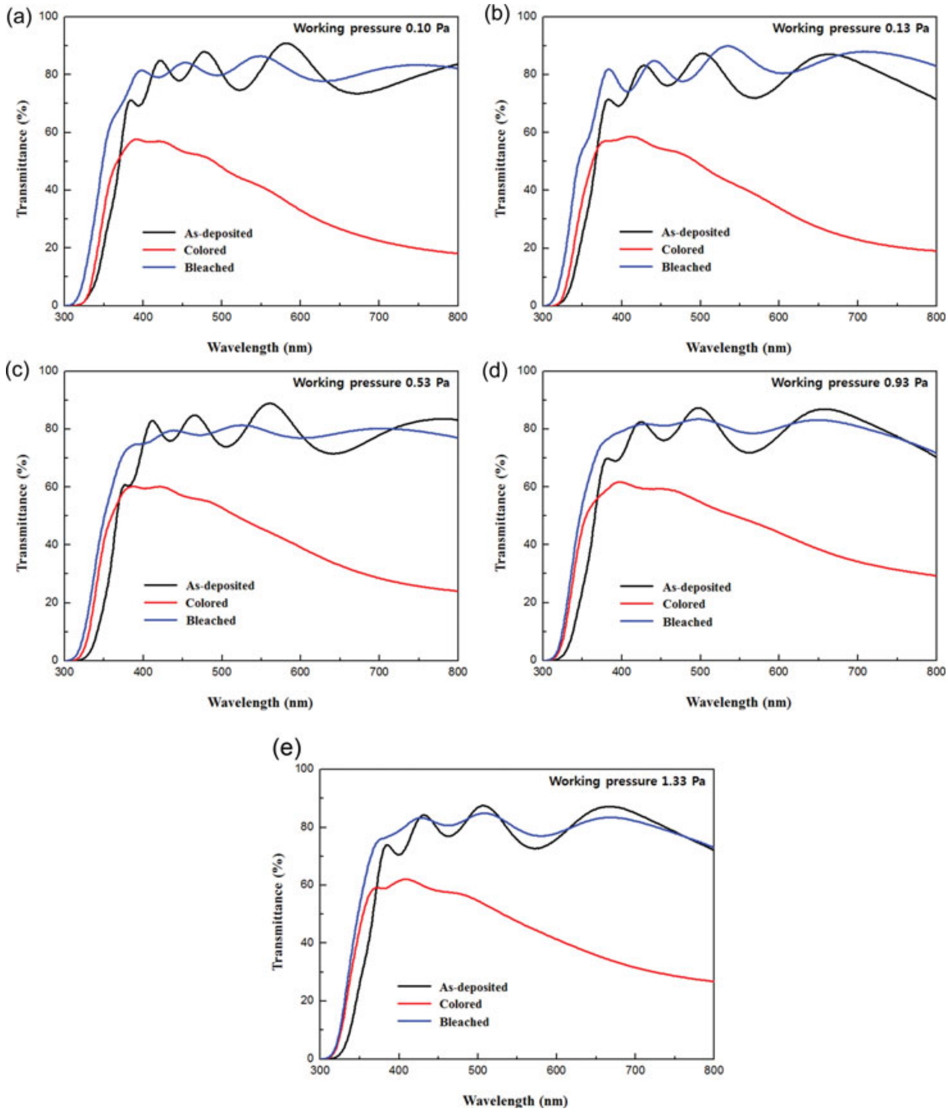

Figure 4. Optical transmittance of WO_{3-x} thin films.

owing to the effect of an external voltage, and it can be changed back to the original state by a reverse external voltage. The average transmittances of the colored and bleached states in the visible range were (36/81%), (37/83%), (41/79%), (45/80%), and (43/80%) at working pressures of 0.10, 0.13, 0.53, 0.93, and 1.33 Pa, respectively. Figure 5 shows optical density change (ΔOD), trnansmittance variation (ΔT), Charge density (mC/cm^2)of the WO_{3-x} thin films in the visible range. The transmittance variations ($\triangle T$) of the WO_{3-x} thin films were estimated to be 45, 46, 37, 34, and 36%, respectively, and they were determined from the equation

$$\Delta T = T_{\text{bleached}} - T_{\text{colored}},$$

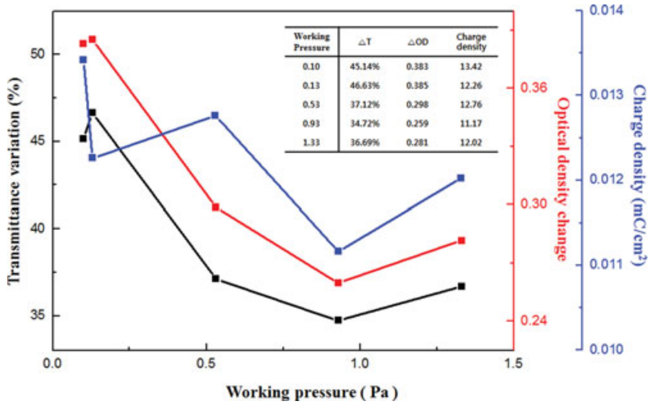

Figure 5. Optical density change (ΔOD), transmittance variation (ΔT), and charge density (mC/cm^2) of the $WO_{3\text{-}x}$ thin films in the visible range.

where T_{bleached} is the transmittance of the thin film in the bleached state and T_{colored} is the transmittance of the thin film in the colored state. The optical density refers to the light absorption ability of EC thin films [18], and the change in OD in the $WO_{3\text{-}x}$ thin films can be determined as

$$\Delta OD = \log\,[T_{\text{bleached}}/T_{\text{colored}}].$$

The $WO_{3\text{-}x}$ thin films deposited at 0.13 Pa was obtained better $\triangle OD$ properties than the other thin films.

Figure 6 shows coloration efficiency (cm^2/C) of the $WO_{3\text{-}x}$ thin films in the visible range. The coloration efficiency of EC thin films is one of the significant parameters for evaluating the practical application of an EC device. It can be determined by the equation

$$CE = OD/Q,$$

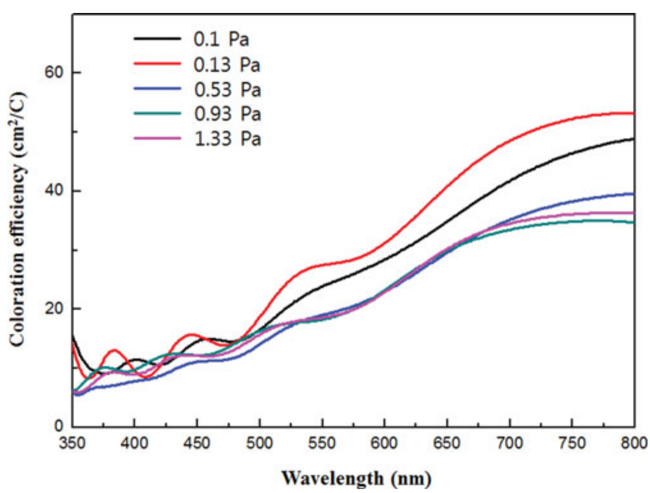

Figure 6. Coloration efficiency (cm^2/C) of the $WO_{3\text{-}x}$ thin films in the visible range.

where Q is the injected charge per unit area. The WO_{3-x} thin films deposited at 0.13 Pa showed the maximum CE value of 31.42 cm^2/C. A high working pressure resulted in smaller mean free path; consequently, the sputtered atoms' energy decreased on account of scattering by collision with Ar gas.

The WO_{3-x} thin films would then become porous thin films. We considered that the difference in density among the thin films originated from the presence of such porous thin films. The coloration efficiency of the WO_{3-x} thin films was observed to decrease with increasing working pressure, showing the correlation between the EC properties of WO_{3-x} thin films and the working pressure.

Conclusions

In this study, WO_{3-x} thin films for EC devices were deposited at an oxygen flow ratio $[O_2/(Ar + O_2)]$ of 0.7 using reactive FTS with variable working pressure. All thin films obtained exhibited amorphous-type diffraction patterns, which might have resulted from the films' amorphous state and internal stress. Therefore, the difference in working pressure did not have any significant effect on the phase. The CVs were recorded at a scanning rate of 30 mV/s between -1.5 and 1.5 V to evaluate the EC performance of the WO_{3-x} thin films. The anodic and cathodic peaks showed obvious symmetry. Transmittance variations ($\triangle T$) of 45, 46, 37, 34, and 36% were obtained for the WO_{3-x} thin films.We consider these differences were due to the varying density of the thin film. The change in optical density of the WO_{3-x} thin films decreased with increasing working pressure. The coloration efficiency of the WO_{3-x} thin film deposited at 0.13 Pa had a maximum value of 31.42 cm^2/C, suggesting its potential for application in the manufacture of EC devices.

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