Effect of sputtering gas pressure on the performance of WO$_3$ thin films electrochromic device

Lin Zhao$^{1,*}$, Shipai Song$^1$ and Le Li$^1$

$^1$School of Materials and Energy Engineering, University of Electronic Science and Technology of China, Chengdu, 611731, China
$^*$email: zhaolin316@uestc.edu.cn

Abstract. WO$_3$ films were deposited on transparent conductive indium tin oxide (ITO) glass under different working pressure conditions via radio frequency magnetron sputtering technology, and their electrochromic properties were studied. The morphology, electrochromic cyclic voltammetry characteristics, and light modulation properties of the films were studied using a scanning electron microscope, an electrochemical test station, and an ultraviolet-visible spectrophotometer. The transmittance modulation amplitude increases first and then decreases with the change of sputtering gas pressure, reaching the maximum transmittance modulation amplitude at 1.0 Pa. For the response time, the increase in sputtering gas pressure also shows a change of shortening and then increasing. By comprehensively considering the stability of the transmittance modulation amplitude and the stability of the response time, it can be found that as the sputtering gas pressure increases, the stability of the device's electrochromic performance increases first and then decreases. Therefore, the sputtering gas pressure needs to be maintained in a relatively reasonable range. When it is too high or too low, it is not conducive to achieving good stability.

1. Introduction
Electrochromic film materials are widely used in smart windows, displays and anti-glare rearview mirrors due to their low power consumption, large light adjustment range, and good memory. Electrochromic thin film materials usually form an electrochromic device with an electrolyte layer, a transparent electrode layer, and an ion storage layer. According to the corresponding relationship between the discoloration process and the charge and discharge process, electrochromic materials can be divided into two types: anode coloring and cathode coloring. As a typical cathode colored electrochromic material, WO$_3$ thin film has been widely studied because of its advantages of wide light adjustment range, high color-changing efficiency and good cycle reversibility.

The electrochromic properties of the WO$_3$ film are greatly affected by the preparation method. There are many methods for preparing WO$_3$ discolored films, including magnetron sputtering [1], pulsed laser deposition [2], thermal evaporation [3], sol-gel [4], spray pyrolysis [5], and anodizing [6] etc. The optimization of WO$_3$ film properties is also based on these methods [7]. Among them, the magnetron sputtering method is easy to prepare the WO$_3$ amorphous film with few defects and high coloring efficiency. The amorphous structure is a key factor for the electrochromic effect of WO$_3$ color-changing films [8]. In addition, magnetron sputtering can be prepared at room temperature, and the substrate material is not required. References [9,10] studied the composition structure and electrochromic characteristics of WO$_3$ amorphous films prepared by reactive magnetron sputtering metal tungsten...
targets, but the effects of process parameters, film composition structure and electrochromic characteristics were not systematically analyzed. The literature [11] studied the relationship between the sputtering pressure of WO3 electrochromic thin film and the response time and optical characteristics of the film's discoloration time, but the cyclic voltammetry characteristics of the film were lacking.

In this paper, WO3 is deposited on ITO transparent conductive glass via magnetron sputtering technology. At the same time, a new method is used to assemble an electrochromic device based on WO3 film. By applying a voltage, the device can be realized in a transparent state and reversible cyclic transition of the colored state (blue). The morphological structure and electrochromic properties (transmittance, transmittance modulation amplitude, response time, CV cycle, and cycle stability) of the WO3 film at the core layer of the electrochromic device are mainly limited by the process parameters of the film preparation. The working pressure of the cavity will affect the film in terms of film formation rate, film density, crystalline properties and flatness. This paper mainly studies the effect of sputtering gas pressure on the performance of WO3 thin films and WO3 based electrochromic devices.

2. Experiment
The thin-film sample was prepared by Radio frequency (RF) magnetron sputtering. The instrument used was JGP560 ultra-high vacuum magnetron sputtering system. The WO3 target is 60 mm * 4 mm, and the sputtering power is 100 W. The substrate is clean and transparent conductive ITO glass, and its square resistance is 12 Ω / □. The vacuum degree of the chamber before coating is pre-pumped to 5 × 10^-4 Pa or less. The sputtering atmosphere is a mixed gas atmosphere of argon and oxygen (Ar : O2 = 50 sccm : 50 sccm). The substrate temperature during the sputtering process was room temperature. The sputtering process pressures are 0.5, 1.0, 1.5, and 2.0 Pa, respectively, and the sputtering time is 120 min.

In this experiment, lithium carbonate (LiCO3) and propylene carbonate (PC) are mixed at 1.5 mol : 1 L and stirred for 2 hours to form 1.5 mol/L LiCO3-PC. Figure 1 is the structural diagram and the physical diagram of the electrochromic device. In the middle of the device sandwich, a PVC plate is used to build an electrolyte tank, and the edge of the plate is opened as a liquid injection port. The edge is sealed with UV curing glue to prevent liquid leakage. Then, the prepared electrolyte is injected with a syringe, and sealed with a UV curing glue to complete the assembly of the entire device.

The Inspect F50 scanning electron microscope (SEM) was used to study the microscopic surface morphology of the thin film samples; the Cary 5000 UV-Vis-NIR ultraviolet-visible spectrophotometer was used to analyze the visible light range of the film; the CH1660d electrochemical test station Cyclic voltammetry was performed on the samples, and the scan rate was 100 mV/s.

3. Result and discussion
Figure 2 is a SEM image of WO3 series thin films with sputtering pressures of 0.5 Pa, 1.0 Pa, 1.5 Pa, and 2.0 Pa at 40, 000 and 160,000 times, scales of 3 μm, and 500 nm, respectively. Observing Figure 2(d), it was found that when the sputtering pressure is 2.0 Pa, the flatness of the film surface is very good, and the particle size distribution is very uniform. Generally speaking, increasing the sputtering pressure can increase the flatness of the film, and the particle size of the film is refined and its distribution tends to be uniform. According to our previous analysis of the impact of sputtering gas pressure on thin films, the reason for this phenomenon may be that as the sputtering gas pressure increases, the scattering of
film-forming particles is strengthened, reducing their energy. The decrease of energy will reduce the diffusion strength of particles on the surface of the substrate, affecting the nucleation and growth of the particles, the compactness of the film, and the uniformity of the particles. In addition, it can be seen from Figure 2(a) that the WO₃ film with a sputtering pressure of 0.5 Pa has obvious abnormal particle growth. The cause of this phenomenon may be that the plasma density is too small, which leads to the formation of film-forming particles. Very large free path and energy. After flying to the substrate and adsorbing it, the particles that arrive first tend to form a strong attractive nucleation center, and the particles that arrive later are due to their larger diffusion strength and the attraction continues to converge to the strong nuclear center, eventually causing the abnormal growth of particles.

Figure 2 SEM images of WO₃ films with different sputtering pressures: (a) 0.5 Pa; (b) 1.0 Pa; (c) 1.5 Pa; (d) 2.0 Pa.

By analyzing the device transmittance curves of the WO₃ series thin films with gas pressures of 0.5 Pa, 1.0 Pa, 1.5 Pa, and 2.0 Pa in Figure 3(a), it can be seen that the transmittance of the transparent devices under different sputtering pressure is basically maintained above 70 T% in the range of 400 nm to 800 nm. In the colored state, as the sputtering pressure is continuously increased, the transmittance performance of the device in the colored state increases first and then decreases, and when the sputtering pressure is 1.0 Pa, the transmittance of the sample is the lowest. Figure 3(b) shows the relationship between the transmittance modulation amplitude and gas pressure at the observation wavelength of 700 nm. It can be found that when the sputtering gas pressure is 0.5 Pa, the modulation amplitude is about 52 T%. Then, when the sputtering gas pressure reached 1.0 Pa, the modulation amplitude rose to around 58 T%, and then it slowly decreased again. The overall transmittance modulation amplitude increases first and then decreases with the change of sputtering gas pressure, reaching the maximum transmittance modulation amplitude at 1.0 Pa. It may also be because when the sputtering gas pressure is too low, the element ratio of W and O deviates too much from the normal value of WO₃, which seriously affects the coloring effect. When the gas pressure is too high, it will affect the diffusion of film-forming particles on the substrate, making it difficult to form WO₃ with a good structure, and then affecting the color rendering properties.
Figure 3 shows the response time graph of the device at the observation wavelength of 700 nm. It can be seen that when the sputtering gas pressure is 1.0 Pa, the coloring and bleaching response times of the devices reach a relatively low value in this group of samples, which are 13.56667 s and 3.11667 s, respectively. Generally speaking, the increase in sputtering gas pressure causes the coloring and bleaching bleaching response time to decrease first and then increase. This may be because when the sputtering gas pressure is too low, the density of the film is relatively large, so the transmission channel left for Li$^+$ is relatively "narrow", which makes it difficult to extract and embed Li$^+$, which causes an increase in response time. When the sputtering pressure is too high, the response time is relatively large. This may be because the excessively high sputtering pressure reduces the energy of particle adsorption and diffusion, resulting in poor film adhesion and affecting the microstructure of the film.

Figure 4 CV cycle diagram of WO$_3$ films with different pressures at a wavelength of 700 nm: (a) 0.5 Pa; (b) 1.0 Pa; (c) 1.5 Pa; (d) 2.0 Pa.
It can be observed from Figure 4 that when the sputtering gas pressure is 0.5 Pa and 2.0 Pa, the area enclosed by the curve is relatively small, indicating that the current density involved in the electrochromic cycle of the device under the two sputtering gas pressures is small. This may be due to the severe scattering of the sputtered particles when the gas pressure is too high, and the low plasma density when the gas pressure is too low will result in less Ar\(^+\) bombarding the target, resulting in very low deposition efficiency, resulting that the charge participating in the reaction low density. In addition, the higher density of the WO\(_3\) film at 2.0 Pa affects the transport of lithium ions.

It can be seen from the transmittance difference curve in Figure 5(a) that in the transparent state, the difference of the device at 2.0 Pa is the largest, which is basically about 5 T\%, and the stability is the worst. In addition, in the wavelength range of 400 nm to 600 nm, the device at 0.5 Pa also has a large difference, even reaching 12.5 T\% at a wavelength of 450 nm. This may be due to the excessively low pressure leading to the denseness of the film, which makes Li\(^+\) difficult to enter and withdraw. After a number of working cycles, a certain amount of lithium ions are accumulated in the film to form tungsten bronze, making the film unable to reach a good transparent state. When the sputtering gas pressure is too high, the adhesion of the film is poor, and frequent Li\(^+\) de-intercalation processes cause damage to the structure. In the colored state, except for the device at 2.0 Pa, which has a large difference in transmittance, the difference of other devices under each sputtering pressure is relatively small and the stability is good.

From Figure 5(b), it can be found that when the sputtering gas pressure is 1.0 Pa, the maximum modulation amplitude can be obtained, and the overall modulation amplitude appears to increase first and then decrease. As can be seen from the modulation amplitude difference curve before and after the cycle in Figure 5(c), the modulation amplitude of the device at 2.0 Pa has a large change, reaching 5T\%, and the devices under other sputtering pressure conditions remain relatively good transmittance modulation amplitude stability. This may be due to the large diffusion energy of the film-forming particles under low pressure, which causes the film to be too dense, making Li\(^+\) difficult to enter and escape, and accumulated in the film after multiple working cycles. When the pressure is too high, the adhesion will be reduced, and the frequent Li\(^+\) de-intercalation process will cause the WO\(_3\) structure to be damaged, which is consistent with the previous analysis.
Figure 5 Transmittance curves and response time plots of WO₃ films at the different sputtering pressures. (a) Transmittance curve graph; (b) Transmittance modulation amplitude graph of the device at a wavelength of 700 nm; (c) Change graph of the device response time at a wavelength of 700 nm; (d) The coloring time of the devices; (e) The response time difference curve of the devices.

It can be seen from Figure 5(d) that the coloring time of the devices under each sputtering pressure is relatively long, maintained above 15s, and the coloring time of the device at 2.0 Pa even reaches 15 s. In the bleaching phase, the response time of the devices at 0.5 Pa and 2.0 Pa was relatively long, reaching 8.455502 s and 9.58522 s. Figure 5(e) also shows the response time difference curve of the devices at various pressures before and after the cycle. Generally speaking, the difference is relatively small, and the device at 1.0 Pa pressure has the relatively best response time stability. This can be explained by the low pressure that brings greater kinetic energy to the film-forming particles, which leads to an increase in the density of the film, a strong confinement effect on Li⁺, and a blocking of the Li⁺ transport channel. When the sputtering gas pressure is too high, the sputtered particles are strongly scattered and have too low energy, which results in poor film adhesion and is not conducive to forming a stable structure. In general, the sputtering gas pressure needs to be kept in a relatively reasonable range. When it is too high or too low, it is not conducive to achieving good response time stability.

4. Summary
In this paper, the effects of different sputtering gas pressures (0.5 Pa, 1.0 Pa, 1.5 Pa, and 2.0 Pa) on the morphology of WO₃ thin films and the performance of electrochromic devices were studied via RF magnetron sputtering. The transmittance modulation amplitude increases first and then decreases with the change of sputtering gas pressure, reaching the maximum transmittance modulation amplitude at 1.0 Pa. For the response time, the increase in sputtering gas pressure also shows a change of shortening and
then increasing. By comprehensively considering the stability of the transmittance modulation amplitude and the stability of the response time, it can be found that as the sputtering gas pressure increases, the stability of the device's electrochromic performance increases first and then decreases. Therefore, the sputtering gas pressure needs to be maintained in a relatively reasonable range. When it is too high or too low, it is not conducive to achieving good stability.

References
[1] C. G. Granqvist: Electrochromic tungsten oxide films: Review of progress 1993–1998, Sol. Energ. Mat. Sol. C. Vol. 60 (2000), p. 201-262.
[2] C. G. Granqvist, in: Handbook of Inorganic Electrochromic Materials, Amsterdam: Elsevier (1995).
[3] S. K. Deb: Opportunities and challenges in science and technology of WO₃ for electrochromic and related applications, Sol. Energ. Mat. Sol. C. Vol. 92 (2008), p. 245-258.
[4] B. W. Faughnan, R. S. Crandall and M. A. Lampert: Model for the bleaching of WO₃ electrochromic films by an electric field, Appl. Phys. Lett. Vol. 27 (1975), p. 275-277.
[5] B. Baloukas, J. M. Lamarre and L. Martinu: Electrochromic interference filters fabricated from dense and porous tungsten oxide films, Sol. Energ. Mat. Sol. C. Vol. 95 (2011), p. 807-815.
[6] A. Rougier, K. Sauvet and L. Sauques: Electrochromic materials from the visible to the infrared region: an example WO₃, Ionics Vol. 14 (2008), p. 99-105.
[7] Y. Baek and K. Yong: Controlled Growth and Characterization of Tungsten Oxide Nanowires Using Thermal Evaporation of WO₃ Powder, J. Phys. Chem. C Vol. 111 (2007), p. 1216-1218.
[8] B. Munro, S. Kramer, P. Zapp and H. Krug: Characterization of Electrochromic WO₃-Layers Prepared by Sol-Gel Nanotechnology, J. Sol-Gel Sci. Techn. Vol. 13 (1998), p. 673-678.
[9] S. R. Bathe and P. S. Patil: Titanium doping effects in electrochromic pulsed spray pyrolyzed-WO₃ thin films,, Solid State Ionics Vol. 179 (2008), p. 314-323.
[10] J. Z. Ou, S. Balendhran, M. R. Field and D. G. Mcculloch: The anodized crystalline WO₃ nanoporous network with enhanced electrochromic properties, Nanoscale Vol. 19 (2012), p. 5980-5988.
[11] D. F. Ding, Y. Y. Cao, Y. W. Liu and Y. Shen: Research progress on electrochromic performance optimization of tungsten oxide film, China Ceramics Vol. 46 (2010).