Improved the response time of WO₃ thin film by deposition of Ag nanolayers

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Abstract. The effects of different Ag layer thicknesses on the optical properties of WO₃-Ag-WO₃ composite films are studied by magnetron sputtering. The research of WO₃-Ag-WO₃ composite films reveals that the introduction of Ag layer is not conducive to improving the transmittance ability of the film, and the transmittance modulation amplitude decreases with the increase of Ag layer thickness. However, with the increase of the Ag layer thickness, the response time and the cycle stability of the films have been significantly improved. However, electrochromic performances will decline when Ag was sputtered too long. Taken together, in this experiment, when the sputtering time of Ag layer is about 6min, the electrochromic device assembled by composite thin film can obtain the most excellent electrochromic performances.

1. Introduction
Tungsten oxide (WO₃) is a typical multifunctional semiconductor oxide. It has a broad application prospect in the fields of colour-changing smart windows [1], gas sensors [2], and photocatalytic electrodes [3]. There are many methods for preparing WO₃ thin films, which can be roughly divided into physical and chemical methods. Among them, physical methods include thermal evaporation method [4], magnetron sputtering method [5], and pulsed laser deposition method [6]. Methods include methods such as chemical vapor deposition (CVD) [7], and sol-gel (Sol-Gel) [8]. Generally, the WO₃ films obtained by different preparation methods have different microscopic morphologies, component structures, and properties, and each has different application fields. The different morphologies can greatly improve the electrochromic, photochromic, and photocatalytic activity of WO₃ thin films. The surface micro-morphology of WO₃ film is one of the key factors determining the film performance. Films with a uniform array of specific micro-topography will also significantly improve their performance [9]. Therefore, how to effectively control and grow a uniform thin film with a specific micro-morphology and array is an important research content of the current WO₃ thin film. Magnetron sputtering is a commonly used physical method for depositing thin films. During the sputtering process, the crystal lattice and molecular structure of the target may be damaged. The sputtered particles can even be as small as the atomic level, and it is easy to form defect structures. In addition, magnetron sputtering is also easy to implement multi-component composite films in a physical and controllable manner.

Among the conductive materials, metallic Ag is relatively inexpensive, but at the same time the electronic conductivity is relatively high. Moreover, metal Ag is used for electrocatalysis in many scenarios. On the other hand, the forbidden band width of WO₃ film is 2.6 eV ~ 3.6 eV, while the nanoscale Ag surface plasmon resonance peak is around 2.9 eV, which is very close to it. Utilizing these
characteristics, a series of experiments on the modification of the Ag layer are designed in this paper to study the effects of the introduction of the Ag layer and the thickness of the Ag layer on the performance of WO\textsubscript{3} and WO\textsubscript{3} based electrochromic devices, and to explore its mechanism. The thin film sample is prepared in the form of a sandwich. First, a layer of WO\textsubscript{3} is sputtered on an ITO conductive glass substrate, then an Ag layer is sputtered, and then a layer of WO\textsubscript{3} is sputtered to form a WO\textsubscript{3}-Ag-WO\textsubscript{3} structure to achieve a WO\textsubscript{3} film improved optical performance.

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 WO\textsubscript{3} 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 : O\textsubscript{2} = 50 sccm : 50 sccm). The substrate temperature during the sputtering process was room temperature. The sputtering process pressure is 1.0 Pa. After the deposition of WO\textsubscript{3}, Ag was continuously deposited from an Ag target by RF magnetron sputtering. The RF working power was 30 W and the gas pressure was increased to 2.0 Pa with the Ar gas flow. The substrate temperature was set at room temperature during deposition. For WO\textsubscript{3}-Ag multilayer film (WO\textsubscript{3}-Ag-WO\textsubscript{3}), the deposition time of each layer of WO\textsubscript{3} films is 60 min, and the deposition time of Ag films between WO\textsubscript{3} films is 0 min, 3 min, 6 min, 9 min, and 12 min, respectively. In this experiment, lithium carbonate (LiCO\textsubscript{3}) and propylene carbonate (PC) are mixed at 1.5 mol : 1 L and stirred for 2 hours to form 1.5 mol/L LiCO\textsubscript{3}-PC.

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 CHI660d electrochemical test station Cyclic voltammetry was performed on the samples, and the scan rate was 100 mV/s.

3. Result and discussion
In order to observe the distribution of Ag on the surface of WO\textsubscript{3}, a layer of WO\textsubscript{3} was deposited on the ITO glass, and then a layer of Ag was deposited to form the structure of WO\textsubscript{3}-Ag. As shown in Figure 1, it is an SEM surface and cross-sectional observation image of a WO\textsubscript{3}-Ag structure film. It can be seen from the figure that snowflake-shaped Ag particles are uniformly distributed on the surface of the WO\textsubscript{3} layer.

As shown in Figure 2 (a), the transparent state transmittance test results of WO\textsubscript{3}-Ag-WO\textsubscript{3} composite films with different thickness of Ag layer are shown by spectrophotometer. The introduction of Ag layer and the increase of its thickness are not conducive to the improvement of the transmittance. This can be attributed to the strong absorption and reflection of light by the Ag layer, which results in the change of optical properties of the composite films. By analyzing the change trend of the curve, we found that the decrease of the transmittance of the device in the colored and transparent States is not positively related to the thickness of the Ag modified layer. This is mainly due to the impact of our test methods. Because, applying voltage to the device to change color and then removing the voltage, the transmittance of the
device will return to a relatively stable value, and the recovery speed of different devices is different. In this paper, when testing the transmittance of electrochromic devices, we choose to add voltage and then turn off the power for 60 s, and then test the transmittance of the coloring state. The addition of Ag can improve the electronic conductivity and ionic conductivity of the device, so it will bring a relatively strong recovery rate and a higher recovery degree. When the thickness of Ag layer is higher, the recovery rate is higher.

Figure 2 Transmittance curves and response time plots of WO3-Ag-WO3 composite films with different thickness of Ag layer. (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

As can be seen from the change curve of the transmittance modulation amplitude with the sputtering time of the Ag layer at the observation wavelength of 700 nm in Figure 2 (b), the modulation amplitude of the device without Ag reaches 62T%. With the increase of the thickness of the Ag layer, the transmittance modulation amplitude decreases continuously. The device with the sputtering time of the Ag layer of 12 min has only 30T% of the transmittance modulation amplitude. This trend may be due to the improvement of the electronic conductivity and ionic conductivity of the device by the addition of Ag, so it will bring a relatively strong recovery rate and high recovery degree, which is consistent with the above analysis. Compared with WO3 thin film device, the coloring time of the device prepared by composite thin film is reduced to less than 10 s, and the fading time is also reduced to a certain extent. This change trend can be seen more clearly from Figure 2 (c). Of course, the decrease of the response time is not proportional to the increase of the thickness of the Ag layer. It can be seen in the figure that the increase of the sputtering time of the Ag modified layer can rapidly reduce the response time of the device. However, when the sputtering time is more than 6 minutes, the response time increases slightly. In general, the response time of coloring and fading decreased first and then increased. The addition of Ag can change the electronic conductivity of WO3 film and increase the electronic transmission rate, and can also change the morphology and structure of WO3 film and increase the transmission rate of Li+, but when the thickness of Ag layer is too high, it will form a certain "barrier" effect on Li+, which will
hinder the transmission of Li\(^{+}\), resulting in the increase of response time. Therefore, the thickness of Ag modified layer should be kept in a relatively reasonable range, not too high or too low.

Figure 3 CV cycle diagrams of the device at 700 nm wavelength. (a) 0 min; (b) 3 min; (c) 6 min; (d) 9 min; (e) 12 min.

Figure 3 shows the CV cycle curve of the devices with different sputtering time of Ag layer at the observation wavelength of 700 nm. Through comparison, it is found that the current density increases continuously with the increase of the thickness of Ag layer, and the maximum current density can be obtained when the sputtering time is 6 min and 9 min, with the overall trend of increasing first and then decreasing. This may be because the introduction of Ag layer increases the conductivity of the film, which is conducive to improving the current density of electrochromic reaction. However, when the Ag layer is too thick, it will hinder the ion conduction and lead to the decrease of current density. In Figure 3 (a), the curve coincidence of different cycles is very poor, and in Figure 3 (b), (c), (d) and (e), except for the first cycle, the curve coincidence is relatively good, showing relatively good CV cycle stability. However, it should be noted that with the increase of the thickness of Ag layer, the reduction peak becomes less and less obvious, and the peak current becomes smaller and smaller.

It can be seen from the transmittance difference curve before and after the cycle in Figure 4 (a), the transmittance of the sample labeled Ag-0 changes greatly after the cycle, and the transmittance difference basically decreases and increases with the increase of the thickness of the Ag layer. Figure 4 (b) and (c) show the transmittance modulation amplitude curves of the devices with different sputtering time of Ag layer under the observation wavelength of 700 nm. With the increase of the thickness of Ag layer, the transmittance modulation amplitude shows a decreasing trend. The stability of the transmittance modulation amplitude increases first and then decreases. The stability is the best when the sputtering time of Ag layer is 6 min.
Figure 4 (a) The transmittance difference curve of the device before and after the cycle; (b) The modulation amplitude curve after the cycle of 700 nm; (c) The difference curve of the modulation amplitude before and after the cycle; (d) The change of the response time after the cycle; (e) The difference of the response time before and after the cycle.

It can be seen from Figure 4 (d) that after 200 working cycles, the response time of color and color fading of devices with different sputtering time of Ag layer decrease first and then increase. After cycling, the coloration and fading time of Ag-0 devices without sputtering Ag layer were 20.1235 s and 8.2333 s, respectively. In addition, the response time difference curve in Figure 4 (e) shows that the response time stability of the device also rises first and then decreases due to the increase of the thickness of the Ag modified layer, which is consistent with the previous analysis. When Ag is added, it can effectively reduce the impedance of the film, increase the concentration of carriers, improve the migration speed of ions and electrons, and effectively shorten the response time of electrochromic devices. Moreover, Ag has certain electrocatalytic effect and improves WO₃ structure performance, which can improve the cycle performance of the device and make the device have better cycle performance.

4. Summary
In this paper, the effects of Ag modified layer on the properties of WO₃ and WO₃ based electrochromic devices are studied by testing and mechanism research of devices with different thickness of Ag layer. Ag has good conductivity. We think that adding Ag modified layer can reduce the impedance of WO₃ film, improve the migration speed of ions and electrons, and shorten the device performance Response time. Moreover, Ag has electrocatalytic activity, which can improve the cycle performance of WO₃ films, and nano scale Ag can adjust the optical properties of WO₃ films. With the increase of the
thickness of Ag layer, the stability of transmittance, the stability of transmittance modulation amplitude and the stability of response time all increased first and then decreased. The experimental results are helpful for the rational design of electrochromic devices in different fields and for the application of the devices.

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