FULL PAPER

Electrochromic properties of WO₃ thin films fabricated by magnetron sputtering, ion plating, and spin coating: A comparative investigation

Kazuki TAJIMA^{1,†}, Hiroshi WATANABE¹, Mizuka NISHINO¹ and Tohru KAWAMOTO^{1,‡}

¹Nanomaterial Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Tungsten trioxide (WO₃) undergoes an electrochromic (EC) color change upon ion exchange via electrochemical redox reactions. Thin films of WO₃ are often fabricated by physical processes based on magnetron sputtering, and lithium is typically used as the cationic species that causes the color change. In a preliminary study, we achieved a suitable EC performance by using potassium as the cation in wet-processed films manufactured by a spin-coating method using WO₃ nanoparticles. However, comparisons of the EC properties of the WO₃ thin films prepared by various techniques are insufficient, and the behavior of potassium in these systems remains unclear. In this study, we observed that it was difficult for potassium to be swept smoothly into films prepared by sputtering or ion plating. In contrast, a wet-processed thin film obtained by spin coating was found to exhibit a good EC performance. This appeared to be largely attributable to structural variations arising from the film preparation methods.

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1. Introduction

Energy-saving windows based on smart window technologies permit dynamic control over light entering buildings, houses, and automobiles and thus hold great promise in terms of energy conservation and lowering environmental impacts.^{1)–4)} Among the relevant technologies, electrochromic (EC) materials allow for electrical control over optical characteristics and are convenient for practical use.^{5)–10)} One important EC material is tungsten trioxide (WO₃), which undergoes a change in its optical characteristics (i.e., a color change) owing to the following electrochemical redox reaction (M = H, Li, K, Na, and so on):

Smart window systems relying on lithium as the cationic species have been put to practical use by major glass companies. The main manufacturing method used for such WO₃ thin films is magnetron sputtering. This technique allows for the production of a highly dense film with nanometer thickness and high controllability by using a vacuum process. However, as this is a batch process, pro-

duction is time consuming and expensive. According to a United States Department of Energy report, high-cost systems are likely only useful in specialty applications.¹¹⁾ Promising research using novel materials and low-cost (e.g., solution-based) manufacturing processes may also have the potential to dramatically reduce costs, and therefore wet (solution-based) processes are likely to become increasingly important. Various researchers are working to develop wet-processing methods for WO₃ materials, but the sol-gel method remains mainstream, and there are situations where commercialization is hindered by the heating required during processing.^{12)–17)}

In our previous work, we investigated the combined use of WO₃ and Prussian blue (PB; Fe₄[Fe(CN)₆]₃) as materials for EC devices in an effort to improve their properties, such as the contrast between the blue and transparent states.¹⁸⁾ The open-framework structures of PB analogues are well known with respect to EC materials. The EC behavior of PB involves three redox states, namely blue (Fe^{III}, Fe^{II}), transparent/colorless (Fe^{II}, Fe^{II}), and green (Fe^{III}, Fe^{III}).¹⁹⁾ The blue color of the mixed-valence species Fe^{III}₄[Fe^{II}(CN)₆]₃ arises from a broad absorption band at approximately 700 nm due to a metal-to-metal charge-transfer transition from the C-coordinated Fe^{II} ions to the N-coordinated Fe^{III} ions via the cyanide ligand. We also found that a water-soluble ink based on dispersed WO₃ nanoparticles could be used to conveniently prepare EC devices with effective EC properties. Especially, PB thin film has a high affinity for potassium, so the WO₃ thin

[†] Corresponding author: K. Tajima; E-mail: k-tajima@aist.go.jp

[‡] Corresponding author: T. Kawamoto; E-mail: tohru.kawamoto@aist.go.jp

film combined with this material is required to have the property of causing a good EC reaction using potassium. However, we have yet to comprehensively evaluate and compare the performance of WO₃ thin films prepared by different manufacturing methods. Furthermore, in previous studies on WO₃ thin-film materials for use in smart windows and other applications, the main cationic species was lithium, whereas the use of potassium has not been investigated. Therefore, in this study, the EC performance of WO₃ thin films fabricated by different manufacturing methods was evaluated from the perspective of using potassium as the cationic species.

2. Experimental

2.1 Fabrication of WO₃ thin films

In this study, we comparatively investigated three kinds of WO₃ thin films fabricated by magnetron sputtering, ion plating, and spin coating. For the sputtering method, glass coated with an indium tin oxide (ITO) thin film with a sheet resistance of approximately 10 Ω/sq. was used as the substrate. A WO₃ thin film with a thickness of 500 nm was deposited by reactive direct-current magnetron sputtering of a 2-in. tungsten metal target of 99.99% purity in a gas mixture of argon and oxygen (7:3). The sputtering power was 70 W and the working pressure was 1.0 Pa. The thin film was prepared at room temperature. For the ion-plated film, a commercially available sample (Geomatec) was used. For the spin-coating method, a procedure using WO₃ nanoparticles was applied. WO₃ powders are typically prepared by sol-gel chemical processes, such as by hydrothermal treatment.^{12)–17)} In this study, we used an aqueous WO₃ slurry containing WO₃ nanoparticles (approximate diameter: 10 nm) supplied by Toshiba Materials. The slurry was concentrated by increasing the solid content to 20 wt %, a level suitable for the spin-coating process. This value was chosen because the film broke when the WO₃ solid content exceeded 20 wt %. Glass coated with an ITO thin film with a sheet resistance of approximately 10 Ω/sq. was again used as the substrate. To fabricate the WO₃ films, this substrate was spin coated with 300 μL of the prepared WO₃ slurry. Spin coating was carried out at 500 rpm for 30 s followed by 1000 rpm for 30 s. In consideration of the future use of heat-susceptible base materials such as resin substrates, no heat treatment step was performed.

2.2 Characterization and evaluation

The WO₃ films were characterized by X-ray diffraction (XRD; D2 PHASER, Bruker) and field emission scanning electron microscopy (FE-SEM; S-4800, Hitachi High-Tech.). The EC properties of the WO₃ thin films were evaluated using an electrochemical analyzer (6115D, ALS/HCH) combined with a UV-vis-NIR light source (DH-2000, Ocean Optics). Cyclic voltammetry (CV) was performed to estimate the peak potentials and peak currents for the anodic and cathodic reversible redox reactions. An Ag/AgCl electrode was used as a reference electrode. The evaluation conditions used for the CV experiments includ-

ed a sweep rate of 5 mV/s, initial potential of 1.0 V vs. Ag/AgCl, maximum potential of 1.0 V vs. Ag/AgCl, and minimum potential of −1.2 V vs. Ag/AgCl; these parameters were selected based on the characteristics of the redox reaction between PB and WO₃ as determined in our previous work.¹⁵⁾ Multiple potential step measurements, transmission spectra, and time strip charts were obtained for response time calculations and cyclic durability testing.

The EC properties of the WO₃ thin films were evaluated using a three-electrode reduction process. The counter and reference electrodes were a Pt wire and saturated calomel electrode, respectively, in a 1.5 mol/L solution of potassium bis(trifluoromethanesulfonyl)imide in propylene carbonate.

3. Results and discussion

3.1 Characteristics of the WO₃ films

Figure 1 shows the XRD patterns of the WO₃ thin films obtained to determine the crystal structure. The peaks at 28.44, 47.3, and 56.12° were excluded during the refinement as they arose from the silicon powder standard (SRM 640e, NIST). Of the WO₃ films examined in this study, the two films fabricated by sputtering and ion-plating possessed amorphous structures. In contrast, the film fabricated by spin coating exhibited all of the major diffraction peaks related to the (002), (020), (200), (120), (−211), (202), (222), and (303) crystal planes of WO₃ oriented in a *P21/n14* monoclinic structure.²⁰⁾ The degree of crystallinity was relatively low because the WO₃ nanoparticles used to prepare the WO₃ thin films have highly amorphous structures.

Figure 2 shows representative FE-SEM images of the surfaces of the WO₃ films. The FE-SEM images reveal that the surfaces were formed by the cohesion of very small nanoparticles. All of the samples exhibited a surface structure resembling an aggregate of nanoparticles. However, as shown in **Fig. 3**, the cross-sectional FE-SEM images of the samples revealed that the films obtained by sputtering and ion plating seemed to form a solid structure, whereas the film prepared by spin coating had a porous structure.

Fig. 1. XRD patterns of the various thin WO₃ films developed in this study, by means of spin coating (green), ion-plating (blue), and sputtering (red).

Fig. 2. FE-SEM surface images of WO_3 films on ITO/glass substrates fabricated by (a) magnetron sputtering, (b) ion plating, and (c) spin coating.

Fig. 3. FE-SEM cross-sectional images of WO_3 films on ITO/glass substrates fabricated by (a) magnetron sputtering, (b) ion plating, and (c) spin coating.

This difference would depend on whether a physical or chemical process was used.

In addition, when films are formed using a physical process to ensure the quality of the porous film in high-pressure conditions, the processing time is prolonged and the ITO/glass substrate must be exposed to the plasma for

an extended period, resulting in thermal damage of the substrate. In previous studies, when we used a flexible polymer-based material as a substrate and long processing times for WO_3 film formation, the substrate was found to be susceptible to plasma damage. With such a method, it is difficult to develop a high-throughput and low-cost

Fig. 4. CV curves of WO₃ thin films obtained by (a) magnetron sputtering, (b) ion plating, (c) spin coating, and (d) comparison of three films.

process. However, as the spin-coating method can be performed at room temperature and atmospheric pressure, the amount of energy input into the base material is reduced, and it can be allowed to dry naturally, making it an extremely convenient method. The film formation method can therefore exert a considerable influence on the film structure.

3.2 EC properties of WO₃ thin films

Figure 4 shows the CV curves of the WO₃ thin films, obtained in this work. The application of a potential of -1.2 V to the WO₃ thin films resulted in a blue-colored state, whereas the application of a potential of 1.0 V afforded a transparent state. It was observed that the current did not flow well in the films formed by sputtering and ion plating. In contrast, effective current–voltage characteristics were observed for the spin-coated film.

Figure 5 shows the transmittance spectra of the WO₃ films on ITO/glass substrates obtained using the three fabrication methods. Considering the CV curves shown in Fig. 4, for the film obtained by sputtering, the redox reaction could not proceed in the entire film with the potassium cation electrolyte, and thus the color change was very slight [Fig. 5(a)]. This suggests that the sputtered film cannot smoothly capture potassium with its larger ionic radius than lithium. This result also relates to the film quality observed in the FE-SEM images. In contrast, the porosity of the film produced by spin coating allows potassium to be swept smoothly into the film as a cation, and the optical properties of the film were also found to change dynamically [Fig. 5(c)].

The films were also examined in terms of their coloration efficiency, which is an important index for evaluating

EC materials. Because the WO₃ film undergoes coloration via cation injection, changes in the optical absorbance can be used as a comparative indicator. The obtained results for the transmittance change (coloring) were converted to absorbance as shown in Fig. 5(d). As an example, the approximate absorbance values of the colored state at a wavelength of 670 nm were 0.2 for the sputtered film, 0.6 for the ion-plated film, and 2.2 for the spin-coated film, indicating that the WO₃ film fabricated by spin coating exhibits the highest EC performance.

Figure 6 shows the relationship between charge and time upon applying a constant voltage to the WO₃ films on ITO/glass substrates obtained using the three fabrication methods. In these plots, we summarize the quantity of charge upon application of a constant voltage, as used previously to evaluate the CV properties. The approximate amount of charge in each film was 8 mC for the sputtered film, 15 mC for the ion-plated film, and 120 mC for the spin-coated film. Therefore, the spin-coated WO₃ film can contain approximately 15 times more charge relative to the sputtered film. In principle, as shown in Eq. (1), because the movement of charges and movement of cations occur simultaneously, the amount of cations swept into the WO₃ film should increase as the charge transfer increases. From the obtained results, the coloring efficiency was calculated to be approximately 25 cm²/C for the sputtered film, approximately 40 cm²/C for the ion-plated film, and approximately 18.3 cm²/C for the spin-coated film. The differences result from the change in the injected charge. The amount of change in absorbance may be reduced when the WO₃ thin film exceeds a certain amount of charge. In order to clarify the mechanism of the variation in coloration efficiencies, it will be valuable to analyze in

Fig. 5. Transmittance spectra of WO_3 films on ITO/glass substrates fabricated by (a) magnetron sputtering, (b) ion plating, and (c) spin coating; (d) absorbance spectra of the three films.

Fig. 6. Relationship between charge and time upon applying a constant voltage to WO_3 films on ITO/glass substrates fabricated by (a) magnetron sputtering, (b) ion plating, and (c) spin coating.

detail the charge quantity using potassium and the distribution of potassium in these films. Various methods such as energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray-fluorescence, and Rutherford backscattering spectrometry may be suitable for evaluating the physical properties of these films, but it is particularly difficult to determine the behavior of the oxygen atoms in the oxide. For example, in compositional analysis using XPS, WO_3 is reduced by the ion etching

used for depth directional analysis, and thus the composition is expected to shift.

In various EC studies on WO_3 systems, although most used lithium-based electrolytes, there have been almost no reports on the use of potassium as the cationic species. The development of such systems would hold great potential in terms of lowering costs and increasing stability and safety, not only for smart windows but also for various other applications such as secondary batteries.

4. Conclusions

In this study, we examined the EC characteristics of WO₃ films from two different perspectives. First, from the viewpoint of manufacturing methods, such films for smart windows are generally fabricated using physical processes like sputtering. Therefore, in this study, we applied a spin-coating method using an aqueous dispersion of WO₃ nanoparticles and evaluated the EC properties of the resulting films against those obtained by physical processing. Second, we investigated the use of potassium as the cationic species. Lithium is generally used as the cationic species in materials for smart windows using WO₃ films, whereas few system based on potassium has been reported prior to this study, to the best of the authors' knowledge. The results showed that, because the potassium could not be swept sufficiently into the sputtered and ion-plated films, the change in transmittance for these films was very small. In contrast, the film manufactured by spin coating had a very porous structure, allowing potassium to be easily swept into the film despite its larger ionic radius than lithium, leading to a dynamic change in transmittance. In addition, the results of these investigations may have implications for the research and development of secondary batteries based on lithium, which have certain limitations related to safety and other aspects and allow the development of potassium secondary batteries using WO₃.

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