

Electrochromic Properties of Crystalline Tungsten Oxide Films Prepared by rf Sputtering

Ryota Takeuchi, Hitoshi Takatsu, Kazuo Urabe and Michihiko Kitao

Research Institute of Electronics, Shizuoka University, Johoku 3-5-1, Hamamatsu 432-8011, Japan

Fax: 053-478-1309, e-mail: romkita@ipc.shizuoka.ac.jp

Crystalline films of tungsten oxide (WO_3) were prepared by rf sputtering method. The effect of crystallization on electrochromic properties was investigated in the visible and near infrared regions. From results of XRD, WO_3 films were found to be crystallized at about 200°C . The structure of crystallized WO_3 was slightly different at the colored and bleached states. As the films were crystallized, optical density change (ΔOD) and coloration efficiency of them decreased in the visible region but both increased in the near infrared region. With increasing injected protons, reflectance of crystalline WO_3 films increased in the near infrared region. Thus, it is concluded that ΔOD and the coloration efficiency of crystalline WO_3 films in the near infrared region were enhanced by reflection.

Key words: electrochromism, tungsten oxide, sputtered film, crystalline film

1. INTRODUCTION

Electrochromic (EC) phenomenon is to give rise to reversible coloration and bleaching by electrochemical injection and extraction of ions and electrons. WO_3 is the most typical EC material. In EC phenomenon of WO_3 , electrochemical reaction has been known to be expressed by the following formula [1],



where M^+ denotes usually H^+ , Li^+ or Na^+ . In the case of crystalline WO_3 films, it was reported that coloration and bleaching mechanism is different from amorphous WO_3 in the near infrared region and due to the modulation of reflectivity [2]. An optical modulation of crystalline WO_3 films is larger than that of amorphous ones in the near infrared region [3]. And the application of crystalline WO_3 films to the smart window is expected to be promising [4]. In the present paper, crystalline WO_3 films were prepared by reactive rf sputtering method and the effect of their crystallization on electrochromic properties was investigated in the region from visible to near infrared.

2. SAMPLE PREPARATION AND EXPERIMENTAL

Samples used in the experiments were conducted by half-cells ($\text{WO}_3/\text{ITO}/\text{Glass}$). Films of ITO were used as the transparent electrode. They were deposited on glass substrates by reactive rf sputtering from a compressed powder ITO target (99.9 % purity). The thickness of ITO films was about 300 nm. WO_3 films were deposited on the ITO films by reactive rf magnetron sputtering from a metal W

Table 1 The preparation conditions of WO_3 films.

		Main sputter
Gas content [%]	Ar	70
	O_2	30
Sputtering time [min]		60
Total pressure [Pa]		8.0
rf power [W/cm^2]		1.28
Substrate temperature [$^\circ\text{C}$]		RT - 300
Film thickness [nm]		250

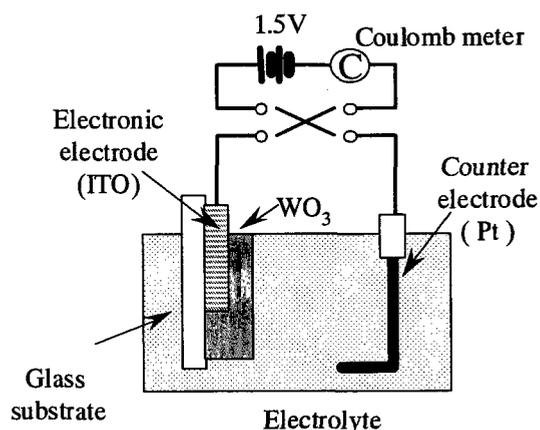


Fig. 1 Experimental set-up of color/bleach cycles.

target (99.9 % purity). Table 1 shows the preparation conditions of WO_3 films. The thickness of WO_3 films was about 250 nm. Structure of WO_3 films was analyzed by the X-ray diffraction.

Fig. 1 shows the experimental set-up of color/bleach cycles. Electrolyte and counter electrode used in color/bleach procedures were 1N- H_2SO_4 ethanol solution and a platinum wire, respectively. DC voltage of ± 1.5 V was applied between ITO film and the counter electrode. The amount of charges injected in the samples (Q) was measured by a coulomb meter.

Transmittance and reflectance spectra of colored and bleached films were measured at wavelengths from 300 to 2500 nm by a spectrometer. In this case, samples were taken out from the electrolyte and dried after the color/bleach procedures. Optical density change (ΔOD) is defined as follows,

$$\Delta \text{OD} = \log(T_B) - \log(T_C), \quad (2)$$

where T_C and T_B denote the transmittance of colored and bleached film, respectively. The coloration efficiency (η) is defined by ratio of ΔOD and the amount of injected charges, namely

$$\eta = \Delta \text{OD}/Q. \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction

Fig. 2 shows XRD patterns of as-deposited WO_3 films prepared at various temperatures of substrates (T_S). The diffraction peaks of 30.6° and 35.4° originated from ITO films. The diffraction peak for WO_3 was not observed for films prepared at $T_S = \text{RT}$ and 100°C . These films are understood to be in amorphous state. When T_S was 200°C , a new diffraction peak was observed at 23.4° , which was assigned to (001) of WO_3 tetragonal. At $T_S = 300^\circ\text{C}$, the intensity of this peak became larger and its full width at half maximum was smaller. It is concluded, therefore, that WO_3 films were crystallized at 200°C and that crystallinity was improved with increasing T_S . After this, the films prepared at $T_S = \text{RT}$ and 300°C will be written as a- WO_3 films and c- WO_3 films, respectively.

XRD patterns of bleached and colored states of c- WO_3 films are shown in Figs. 3 and 4, respectively. In order to investigate in detail the (001) peak of WO_3 tetragonal, the range of 2θ was set between 22° and 25° . As shown in the Fig. 3, a diffraction peak of bleached films was located at 23.4° , which corresponds to the (001) peak of WO_3 tetragonal. The crystal structure of bleached c- WO_3 films is supposed to be the same one as the as-deposited films. As seen from Fig. 4, on the other hand, a new diffraction peak of 23.8° , which corresponds to the (001) peak of

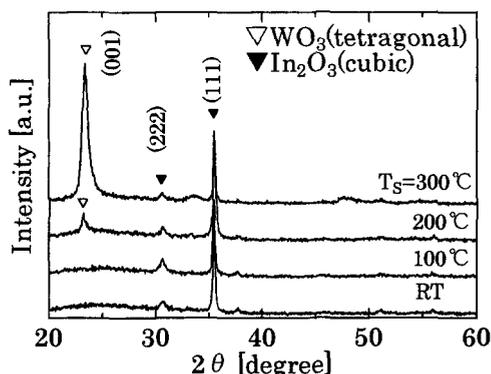


Fig. 2 XRD patterns of as-deposited WO_3 films prepared at various temperatures of substrate.

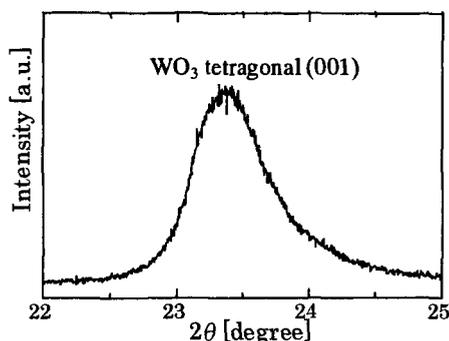


Fig. 3 XRD patterns of bleached films of crystalline WO_3 .

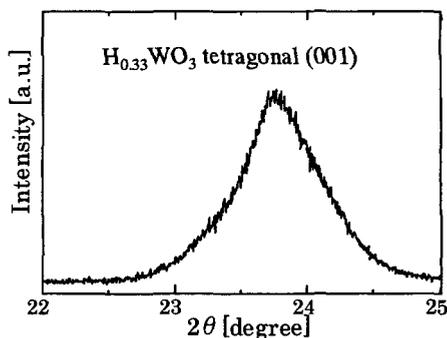
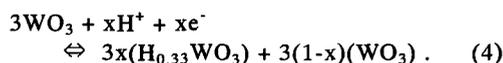


Fig. 4 XRD patterns of colored films of crystalline WO_3 .

$\text{H}_{0.33}\text{WO}_3$ tetragonal, appeared for the colored state. The peak intensity of 23.4° decreased and became the shoulder. Phase of c- WO_3 films is considered to be transferred in part by coloration (the injection of protons). Tungsten bronze in c- WO_3 may be the form of $\text{H}_{0.33}\text{WO}_3$. Thus, electrochemical reaction of coloration and bleaching of c- WO_3 films is supposed as follows,



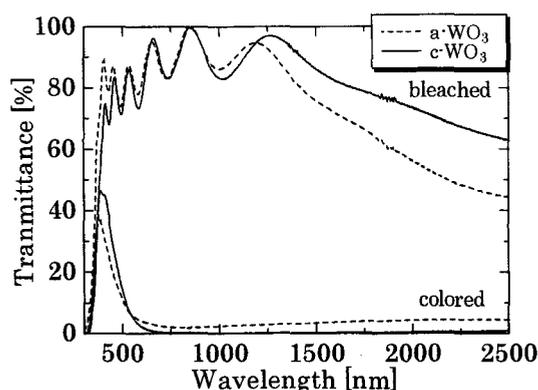


Fig. 5 Transmittance spectra of a-WO₃ and c-WO₃ films.

3.2 Transmittance Spectra

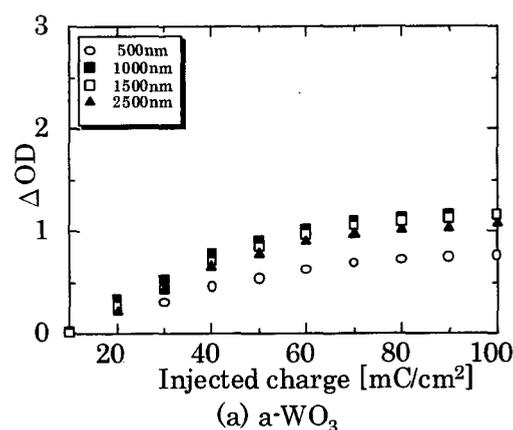
Fig. 5 shows the transmittance spectra at the colored and bleached states of a-WO₃ and c-WO₃ films. The transmittance modulation of c-WO₃ films increased in the near infrared region (1000-2500 nm) but decreased in the visible region (400-600 nm) in comparison with that of a-WO₃ films.

Figs.6 (a) and (b) show ΔOD of a-WO₃ and c-WO₃ films for various wavelengths vs the amount of injected charges, respectively. As shown in the figures, values of ΔOD of c-WO₃ at wavelength of 500 nm were smaller than a-WO₃, but values of ΔOD at other longer wavelengths were larger than a-WO₃. ΔOD increased with increasing injected charges. ΔOD had a tendency to saturate at large amount of injected charges. This is considered to be caused by leakage current through the cells.

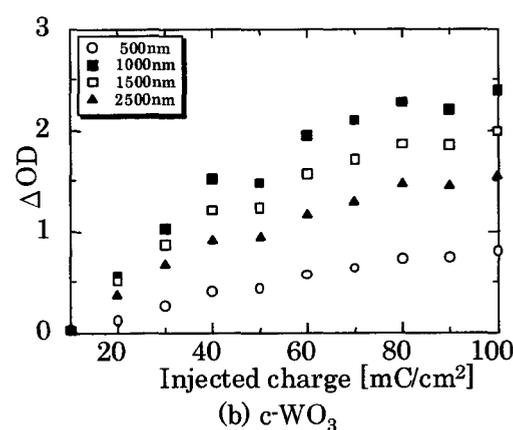
The coloration efficiency η for various wavelengths vs the substrate temperatures is shown in Fig. 7. As shown in the figure, η at wavelength of 500 nm was lower than one at other longer wavelengths. With increasing substrate-temperature, η at wavelength of 500 nm decreased but η at other longer wavelengths increased. At wavelength of 1500 nm, especially, η of the c-WO₃ films could be improved about twice in comparison with a-WO₃ films. Accordingly, crystalline WO₃ films are considered to be more effective than amorphous WO₃ films for EC characteristics in the near infrared region.

3.3 Reflectance Spectra

Figs. 8 and 9 show the reflectance spectra of a-WO₃ and c-WO₃ for various amount of injected charges, respectively. The undulation of reflectance curves in visible region was caused by the interference due to thin layers in the cell. The reflectance of a-WO₃ is low at both colored and bleached states in the region of all wavelengths. The reflectance of c-WO₃, on the



(a) a-WO₃



(b) c-WO₃

Fig. 6 ΔOD of (a) a-WO₃ and (b) c-WO₃ films at various wavelengths vs the amount of injected charges.

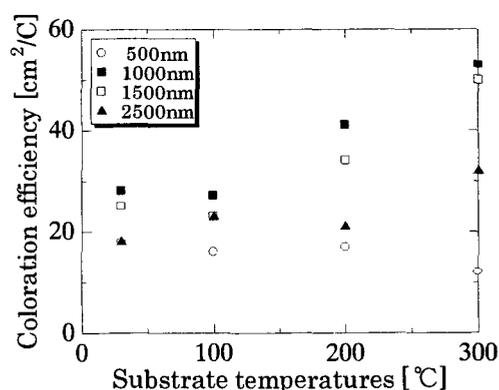


Fig. 7 The coloration efficiency at various wavelengths vs the substrate temperatures.

other hand, increased in the longer wavelength region with increasing the injected charges. In c-WO₃ films there was a cut-off wavelength, at which the reflectance rapidly increased. Moreover, the cut-off wavelength shifts to somewhat shorter wavelength with increasing the injected charges. It was reported that, when

charges were heavily injected into crystalline WO_3 films, the reflectance increased because of total reflection related to the plasma frequency of free carriers [5] and also reported that reflectance increased with increasing substrate-temperature [3]. However, total reflection could not be confirmed by our experiment. The reason speculated is that the surface of sputtered films was not flat and scattered the incident light. As crystallization of WO_3 increases reflectance in the near infrared region, optical modulation is considerably increasing.

4. CONCLUSION

WO_3 films were prepared at various temperatures of substrates by reactive rf sputtering method. The following results were obtained.

- 1) WO_3 films prepared at $T_s = \text{RT}$ were amorphous. WO_3 films prepared at 300°C gave good crystallinity.
- 2) From XRD, the (001) peak of WO_3 tetragonal was observed in as-deposited and bleached states of c- WO_3 films and (001) peak of $\text{H}_{0.33}\text{WO}_3$ tetragonal was observed in colored states of c- WO_3 films.
- 3) In c- WO_3 films, transmittance modulation and ΔOD were large in the near infrared region. With improving crystallinity, coloration efficiency decreased in visible region but increased in near infrared region.
- 4) Reflectance of c- WO_3 films increased in the near infrared region with coloring.

As crystalline WO_3 films have a large optical modulation in the near infrared region in comparison with the amorphous WO_3 films. Crystalline WO_3 films are proven to be promising for smart window.

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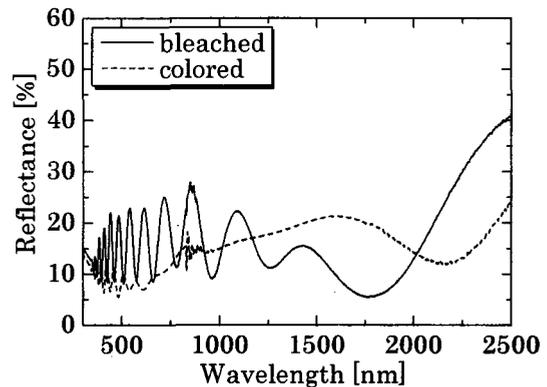


Fig. 8 Reflectance spectra of colored and bleached a- WO_3 film.

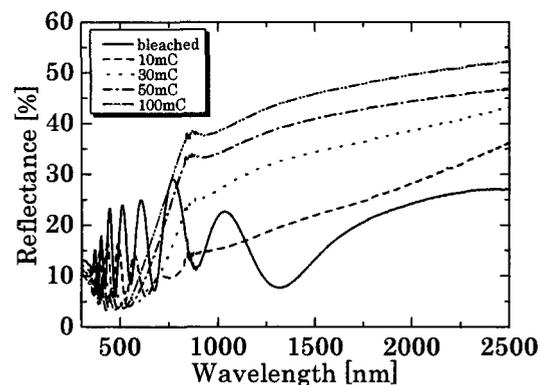


Fig. 9 Reflectance spectra of c- WO_3 film for various amount of injected charges.

(Received January 14, 2002; Accepted April 25, 2002)