Optical and electrochromic properties of RF reactively sputtered WO_3 films

E. Washizu, A. Yamamoto, Y. Abe*, M. Kawamura and K. Sasaki

Department of Materials Science, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido, 090-8507, Japan

Abstract

The effects of deposition conditions, including substrate temperature and sputtering gas pressure, on the optical and electrochromic (EC) properties of WO_3 films prepared by RF reactive sputtering were investigated. The maximum optical band gap energy of 3.15 eV was obtained on a room-temperature substrate temperature, and decreased with increasing substrate temperature. However, the maximum refractive index of about 2.5 was obtained at a sputtering gas pressure of 5 mTorr and a substrate temperature of 500°C, and decreased with decreasing substrate temperature and with increasing pressure. The decrease in bandgap energy and refractive index are thought to have been caused by an increase in WO_3 cluster size and a decrease in film density, respectively. Electrochromic (EC) response times of the WO_3 films were measured in an electrolyte of 1N H_2SO_4 aqueous solution. Fast EC responses were obtained for the WO_3 films with wide band gap energies and low refractive indices. The results indicate that the optical properties of WO_3 films are useful indicators of EC response.

Keywords: Reactive sputtering; WO_3 thin film; Optical properties; Electrochromic

* Corresponding author. E-mail address: abeys@mail.kitami-it.ac.jp

response time

PACS: 68.55.-a; 78.20.C; 78.20.J; 81.15.Cd

1. Introduction

WO_3 thin films are the most common electrochromic (EC) material and have been prepared by a variety of methods, including vacuum evaporation, sputtering, pulsed laser deposition and sol-gel preparations [1]. Reactive sputtering is a method for depositing compound thin films by the sputtering of metal targets in a reactive gas atmosphere and is thought to be useful in the fabrication of WO_3 thin films [2-4]. Since the microstructure, optical and electrical properties as well as the EC characteristics of WO_3 films depend on the preparation conditions, it is important to elucidate the physical properties of the films needed to obtain good EC characteristics. In this study we examine the effects of sputtering conditions, such as substrate temperature and sputtering gas pressure, on the optical and EC properties of WO_3 films, and clarify the relationship between bandgap energy, refractive index and EC response time.

2. Experimental details

WO_3 thin films with thicknesses of 300-800 nm were prepared using an RF magnetron sputtering system. A 99.9% pure tungsten metal target with a diameter of 2-inches was sputtered in mixed gas of argon and oxygen. Total sputtering gas pressure and substrate temperature were varied from 5 to 50 mTorr and from room temperature (RT) to 500°C, respectively. Substrate temperature was stabilized for more than 30 min at each temperature before the deposition of the films. Oxygen gas flow rate and RF power were kept constant at 35% and 50W, respectively. Quartz glass was used as the substrate for optical measurements, while indium tin oxide (ITO) coated glass (Corning #7059) was used for EC measurement. Crystal structure and surface morphology of the deposited WO_3 thin films were characterized by X-ray diffraction (XRD) with Cu Kα radiation and scanning electron microscopy (SEM), respectively. Optical bandgap energy was measured using spectrophotometry, and refractive index was measured using ellipsometry with a He-Ne laser (633 nm). For EC measurements, 1N H_2SO_4 aqueous solution was used as the electrolyte, and Pt and Ag/AgCl were used for counter and reference electrodes, respectively. Coloration and bleaching of the EC cells were carried out by applying DC voltages of –0.4 V and +2.0 V, respectively, with respect to the reference electrode.

3. Results and discussion

First, the structure and surface morphology of the WO_3 films were studied. Figure 1 shows XRD patterns of WO_3 films deposited at various substrate temperatures. The XRD pattern of the film deposited at RT is very broad, which indicates that the structure of the film is amorphous. XRD peaks due to orthorhombic WO_3 crystal are clearly seen at substrate temperatures above 200°C, with the width of the peaks decreasing with increasing substrate temperature, indicating that crystal grain growth is promoted by increasing substrate temperature. The crystallite size normal to the substrate surface calculated using Scherrer's equation increased from 13 nm to 37 nm with increasing the substrate temperature from 200°C to 500°C, and it increases up to 45 nm at 50 mTorr and

500°C. Surface SEM images of the WO_3 films are shown in Fig. 2. The surfaces of the amorphous films deposited onto RT substrates are very flat, while the polycrystalline films deposited at 500°C have rough surfaces. Large crystal grains with diameters of several hundred nanometers are seen on the 500°C film deposited with 50 mTorr sputtering gas. It is thought that lower deposition rate of the WO_3 films enhanced crystal grain growth because the deposition rate decreased from 20 nm/min to 1.1 nm/min with increasing the sputtering gas pressure from 5 mTorr to 50 mTorr. The SEM results correspond qualitatively well with those of XRD measurements, though the crystal grain size obtained from the SEM observation is larger than the crystallite size, or more correctly, the coherent domain size, obtained from the XRD measurement.

Next, optical properties of the WO_3 films were investigated. Figure 3 shows optical bandgap energies of WO_3 films deposited with sputtering gas pressures of 5 mTorr and 50 mTorr as a function of substrate temperature. The optical bandgap energy was estimated from transmittance spectra by assuming that the absorption coefficient α is given by the following equation [5]

$$\alpha = A\,(h\nu - E_g)^2 / h\nu,$$

where A, $h\nu$ and E_g are a constant of proportionality, photon energy and optical bandgap energy, respectively. Oscillations in the low energy region of the transmittance spectrum shown in the inset of Fig. 3 are due to interference effects. To avoid these, bandgap energy was estimated by straight line extrapolation from the high-energy region. Bandgap energy is found to decrease with increasing substrate temperature. The highest bandgap energy of 3.15 eV was obtained for amorphous films deposited at RT. Since the bandgap energy of bulk WO_3 is reported to be 2.62 eV for indirect transitions [5], the larger bandgap energies observed are thought to be the result of quantum size effects due to the small WO_3 cluster size [3]. The lowest bandgap energy of 2.7 eV, which is close to the bandgap energy of bulk WO_3, was obtained for the films with the maximum grain size deposited at 50 mTorr and 500°C, though the scattering of the transmitted light may degrade the accuracy of the optical bandgap energy for the rough WO_3 films. Bandgap energies and their substrate temperature dependence similar to our results were reported for sputtered and thermally evaporated WO_3 films [2, 3, 6], and the results shown in Fig. 3 correspond well with SEM results. Refractive indices of the films are shown in Fig. 4. It can be seen that the refractive index of the WO_3 films increases with increasing substrate temperature, with the highest value of about 2.5 obtained for the films deposited at 5 mTorr and 500°C, and the value is nearly the same as that reported for crystalline WO_3 films prepared by sputtering [2]. It is known that refractive index depends on film density, with films that have lower refractive indices also having lower densities. We assume the Lorentz-Lorenz equation,

$$(n^2-1)/(n^2+2) = N\alpha_p/3\varepsilon_0 \propto \rho,$$

where n, N, α_p , ε_0 and ρ are refractive index, number of dipoles per unit volume, polarizability of dipoles, permittivity of free space and film density, respectively. If a refractive index of 2.5 is assumed for bulk WO_3 [7], the relative film density ρ/ρ_0 can be estimated as 0.67 for the film with the minimum refractive index of 1.8, where ρ_0 is the density of bulk WO_3. In addition, a drop in the refractive index is observed for the films deposited at 500°C and 50mTorr. It is thought to have been caused by the surface layer being a mixture of WO_3 crystal grains and air [8], since the surface of the film is very rough as shown in Fig. 2. The drop may also be caused by the scattering and absorption of the incident laser beam that was used for ellipsometry, because the film was pale yellow and its surface was rough.

Finally, the relationship between the optical properties of the WO_3 films and their EC characteristics are discussed. Figures 5 (a) and (b) show the change of transmittance of EC cells during the coloring and bleaching processes, respectively. The WO_3 films were deposited with substrate temperatures from RT to 500°C in a 50 mTorr sputtering gas. As can be clearly seen, the coloring and bleaching times decrease with decreasing substrate temperature, with the fastest responses obtained for the film deposited at RT. The transmittance of the WO_3 film deposited at 500°C is very low even in the bleached state and the appearance of the WO_3 film is pale yellow and opaque. Light scattering due to large crystal grains is thought to be the reason for the low transmittance, and reaction between ITO and WO_3 films may influence on its EC properties. Results of the optical and EC properties of the WO_3 films are summarized in Fig. 6. The response time t_r in this figure was defined as the time it took for the transmittance to fall to half that of the initial bleaching state. The response times for films with different bandgap energies and refractive indices are plotted. It can be clearly seen that short response times below 1 min are obtained for films with bandgap energies above 3.1 eV and refractive indices below 2.2. The minimum coloration time obtained in this study was 6 sec, which is comparable to that reported for sputtered WO_3 films [9, 10]. These results are quite reasonable because wide bandgaps and low refractive indices mean that the cluster sizes of the WO_3 films are small and the film densities are low. Therefore fast ion diffusion is expected for low density WO_3 films with small cluster sizes. These results suggest that optical properties are useful indicators of EC response.

4. Conclusion

Optical bandgap energies and refractive indices of WO_3 thin films deposited by reactive sputtering were studied. Wide bandgap energy, low refractive index WO_3 films, which are thought to have small WO_3 cluster sizes and low film densities, were deposited using low substrate temperatures and high sputtering gas pressures. Fast EC responses of less than 1 min were obtained for WO_3 films with bandgap energies above 3.1eV and refractive indices below 2.2. These results suggest that optical properties are useful indicators of EC response characteristics.

Acknowledgement

Thanks are due to Dr. H. Itoh of Kitami Institute of Technology for allowing the use of his spectrophotometer.

References

[1] C. G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam (1995) p. 29, 55, and 65.

[2] H. Kaneko, F. Nagao, K. Miyake, J. Appl. Phys. 63 (1988) 510.

[3] T. Kubo, Y. Nishikitani, J. Electrochem. Soc. 145 (1998) 1729.

[4] A. Yamamoto, Y. Abe, M. Kawamura, K. Sasaki, Vacuum 66 (2002) 269.

[5] F. P. Koffyberg, K. Dwight, A. Wold, Solid State Commun. 30 (1979) 433.

[6] K. Miyake, H. Kaneko, M. Sano, N. Suedomi, J. Appl. Phys. 55 (1984) 2747.

[7] S. Sawada, G. C. Danielson, Phys. Rev. 113 (1959) 1008.

[8] H. G. Tompkins, A User's Guide to Ellipsometry, Academic Press, San Diego (1993) p.95.

[9] H. Kaneko, S. Nishimoto, K. Miyake, N. Suedomi, J. Appl. Phys. 59 (1986) 2526.

[10] J. L. He, M. C. Chiu, Surf. Coat. Technol. 127 (2000) 43.

Figure captions

Fig. 1. XRD patterns of WO_3 films deposited at various substrate temperatures (T_s) on quartz glass substrates. The sputtering gas pressure was 5 mTorr.

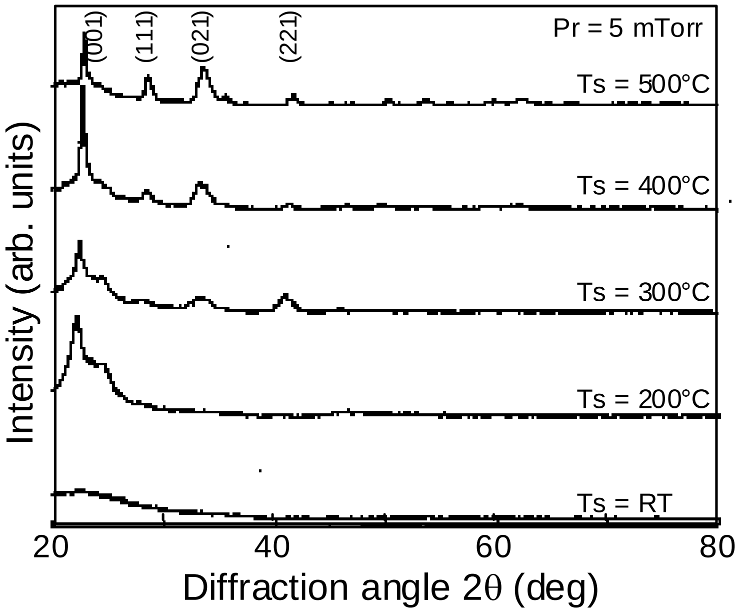
Fig. 2. Surface SEM images of WO_3 films deposited at several substrate temperatures and sputtering gas pressures.

Fig. 3. Optical bandgap energy of WO_3 films as a function of substrate temperature. Open circles and squares are data for the films deposited at 5 mTorr and 50 mTorr, respectively. The inset shows a transmittance spectrum of a WO_3 film deposited at RT.

Fig. 4. Refractive index of WO_3 films as a function of substrate temperature. Open circles and squares are the data for the films deposited at 5 mTorr and 50 mTorr, respectively.

Fig. 5. EC response characteristics of WO_3 films deposited at various substrate temperatures for (a) coloring and (b) bleaching. The sputtering gas pressure was 50 mTorr and the wavelength used in the transmittance measurement was 600 nm.

Fig. 6. The effect of bandgap energy and refractive index of WO_3 films on their EC response times. Response time t_r was defined as the time at which transmittance decreased to half that of the initial bleaching state.



(001)
(111)
(021)
(221)
Pr = 5 mTorr
Ts = 500°C
Ts = 400°C
Ts = 300°C
Ts = 200°C
Ts = RT
Intensity (arb. units)
20
40
60
80
Diffraction angle 2θ (deg)

Fig. 1

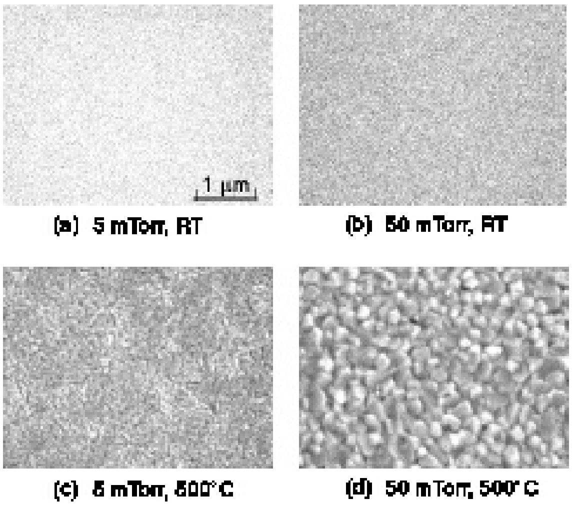


Fig. 2

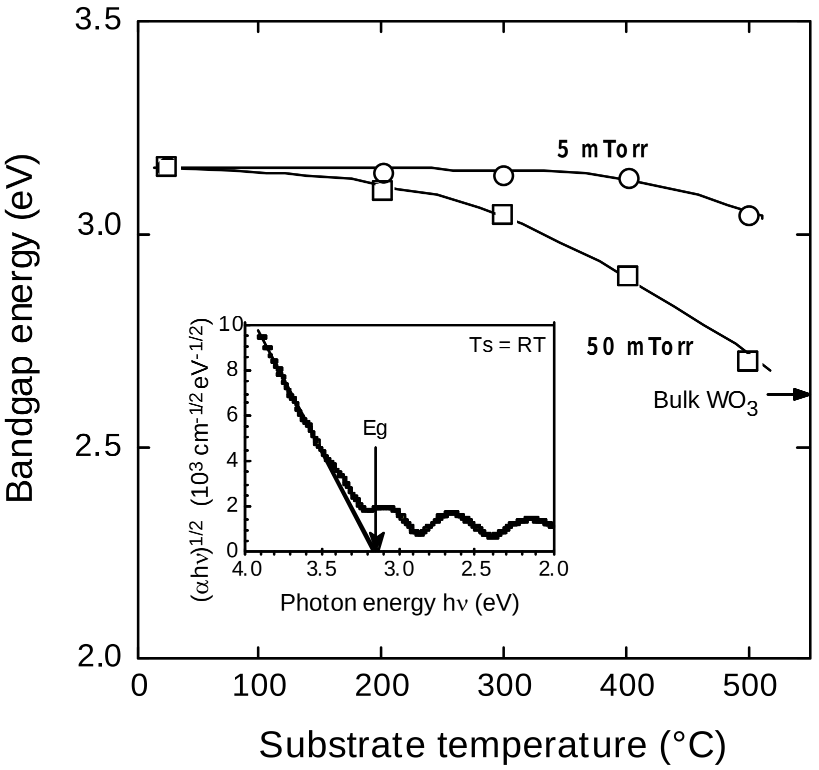

3.5
3.0
2.5
2.0
Bandgap energy (eV)
0
100
200
300
400
500
Substrate temperature (°C)
5 mTorr
50 mTorr
Bulk WO_3
Ts = RT
Eg
$(\alpha h\nu)^{1/2}$ $(10^3\ cm^{-1/2} eV^{-1/2})$
10
8
6
4
2
0
4.0
3.5
3.0
2.5
2.0
Photon energy hν (eV)

Fig. 3

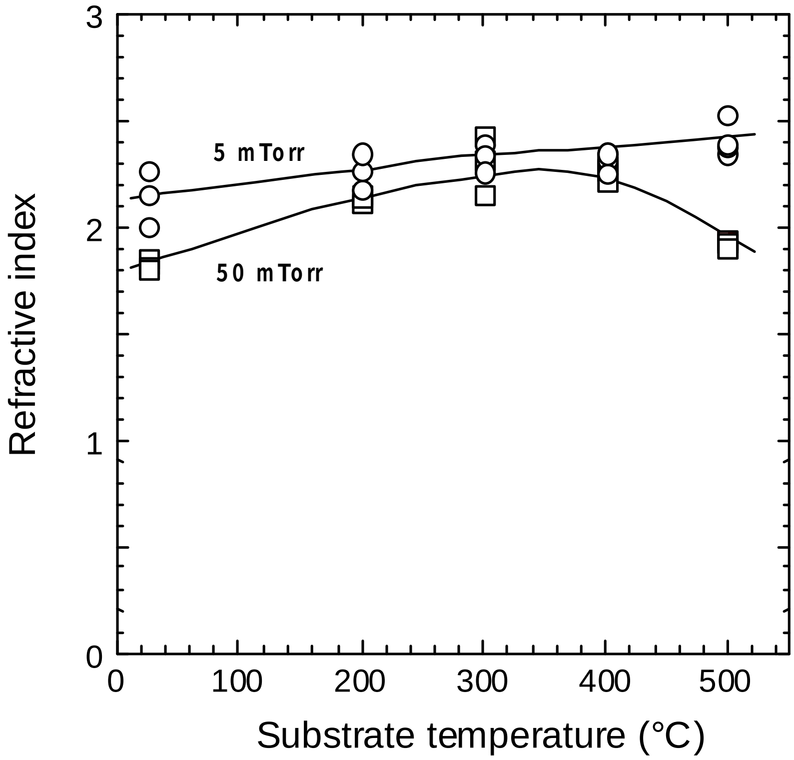
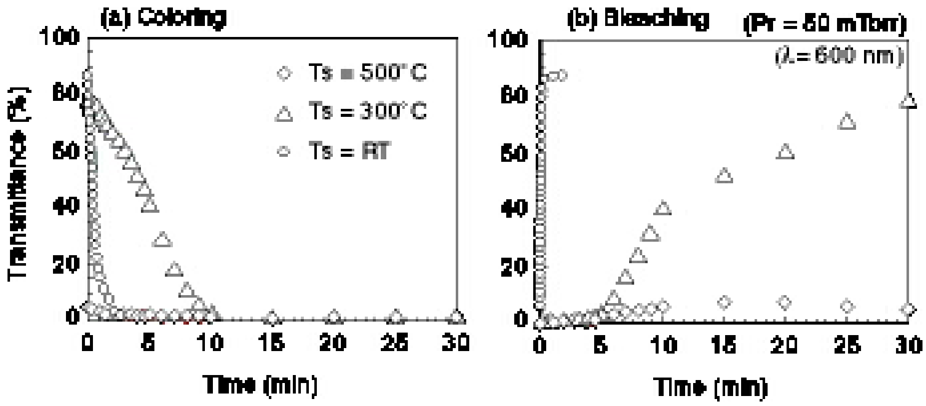

3
2
1
0
Refractive index
5 mTorr
50 mTorr
0
100
200
300
400
500
Substrate temperature (°C)

Fig. 4



(a) Coloring
Ts = 500°C
Ts = 300°C
Ts = RT
Transmittance (%)
Time (min)
(b) Bleaching
(Pr = 50 mTorr)
(λ = 600 nm)
Time (min)

Fig. 5