Preparation of WO_3 Thin Films for Electrochromic Display by Plasma Process

Hiroharu KAWASAKI, Takeaki MATSUNAGA, Weimin GUAN,
Tamiko OHSHIMA, Yoshihito YAGYU, Yoshiaki SUDA
Sasebo National College of Technology, 1-1 Okishin, Sasebo, Nagasaki 857-1193

(Received: 4 September 2008 / Accepted: 27 November 2008)

Tungsten oxide (WO_x) thin film, which is well known as an electrochromic display, was deposited on the ITO film coated flexible substrates using the RF magnetron sputtering method. Phenomena of processing plasmas, the film quality and the electrochromic properties of deposited WO_3 thin film have been studied as parameters of a gas pressure and gas mixture. Experimental results suggest that deposited WO_x thin films at gas pressure of 10 Pa were amorphous structure independent of a gas mixture. XPS analyses suggest that the amorphous type WO_x(x=2.43) film can be deposited at the gas flow ratio of O_2:Ar=5:5, total gas pressure of 10Pa and RF power of 50W. The color of electrochromic display prepared using the deposited WO_x film change from transparent to blue by applying a DC voltage, which means that the deposited film under the condition worked as electrochromic display.

Keywords: Tungsten oxide, RF magnetron sputtering, electrochromic display

1. Introduction

The electrochromic characteristic is a phenomenon in which a color of metal changes with electric chemical reactions [1]. They usually use as an electrochromic display and an optical shutter using the phenomenon. Tungsten oxide (WO_3) is well known as a material with the electrochromic properties [2-11]. Usually, WO_3 thin films as electrochromic display have been prepared on the glass substrates. However, a glass substrate is easily damaged and it cannot be bend. If WO_3 thin film can be prepared on the flexible substrates (PET, PEN etc.), various applications may be performed. Therefore, the technology to prepare at low temperature has been required to prepare WO_3 thin films on the flexible substrates with low heat resistance. We have been prepared the WO_3 thin films using the pulsed laser deposition (PLD) method at low temperature on the flexible substrates [12-14]. Experimental results suggest that WO_3 thin films deposited by PLD method worked as electrochromic display and they show the high transmittance independent of deposition condition [12]. However, uniformity of the films is not high enough for display panel using PLD method.

In this study, WO_3 thin films were prepared on indium tin oxide (ITO) films coated flexible (PEN) substrates using RF magnetron sputtering methods [18-21]. We examined the optical and electrical properties of each thin film, and the electrochromic property of the stacked structure was observed. We also examined crystalline structure and atomic composition rate using X-ray diffraction (XRD) analysis and X-ray photoelectron spectroscopy (XPS), respectively. We studied the suitable conditions to prepare a flexible WO_3 electrochromic display using these experimental results.

author's e-mail: h-kawasa@post.cc.sasebo.ac.jp

2. Experiments

A schematic for film preparation and measuring characteristics of RF plasma is shown in Fig. 1. The deposition chamber (ANELVA: PRF-065B) was evacuated to a base pressure of 4×10^{-4} Pa by a turbomolecular pump and rotary pump, and then filled with the oxygen (O_2:99.99%) and argon (Ar:99.99%) mixture gas at a flow rate of 10 sccm. RF magnetron sputtering plasma was generated at 13.56 MHz in frequency and 50 W in discharge RF power. In this deposition, sputtering target was pure tungsten (W, 99.9%), deposition time was 180min and substrate was room temperature. The substrates in these experiments were ITO films coated flexible substrates (OTEC, Tobi Co., Ltd.) and located at 2.0 cm from the target. The substrates were cleaned using an ultrasonic agitator by repeated bathing and were then rinsed in high-purity deionized water prior to loading into the deposition

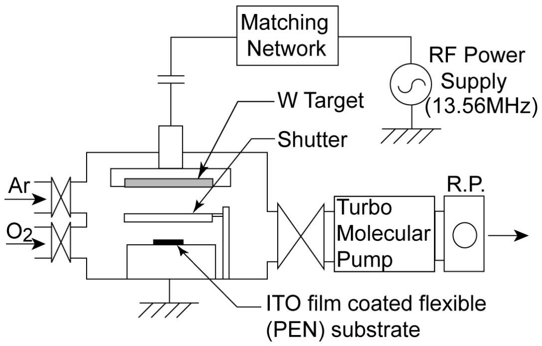


Fig.1 Experimental apparatus.

chamber.

Optical emission spectra were recorded through a spectrometer (Hamamatsu C5095) equipped with an ICCD camera (Hamamatsu C7164-03) after 16 times integration.

The crystalline structure and crystallographic orientation of the thin films were characterized by XRD (RIGAKU; RINT2100V) using a CuKα radiation. The composition of the films was measured by XPS (JEOL; JPS9010). The surface morphology of the films was observed by AFM (JOEL; JSPM4210). Film thickness was measured by α-step (Veeco; Dektak 8). The transmittance of the solution was measured by a Hitachi UV-3300 spectrometer at a wavelength of 550 nm. Deposition conditions are shown in Table 1.

Table 1 Deposition conditions.

Target	W (purity 99.9 %)
Substrate	ITO film coated flexible PEN
Base Pressure	4×10^{-4} Pa
Gas	Ar, O_2 (purity 99.9 %)
Gas mixture	O_2 :Ar=5:5~10:0
Total Gas pressure	3~10 Pa
RF power	50 W
Deposition time	180 min.

3. Results and Discussion

3.1 Optical emission spectra

Figure 2 shows OES of the RF plasma at 10 Pa and O_2:Ar gas mixture in 5:5. Tungsten atoms (W I) and Ar atoms (ArI) can be mainly detected [12]. The OES results showed the presence of mono-atomic neutral tungsten atoms (W I). However, W ions, O neutrals atoms and molecular species are not detected in this condition. Emission peak increased with Ar gas mixture. These results suggest that the oxidation reaction of W was caused on the substrate surface.

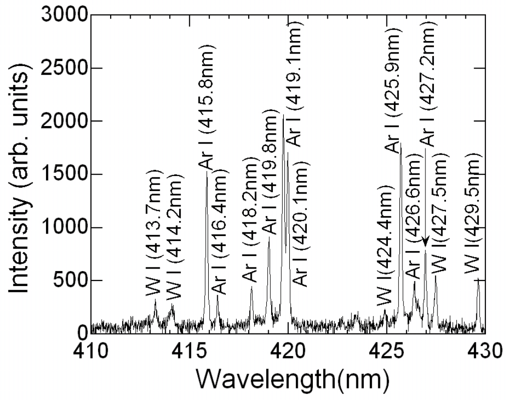


Fig. 2 Optical emission spectrum of RF plasma. RF power:50W, P=10Pa, O_2: Ar =5:5.

3.2 Film quality

Table 2 shows film thickness after 120 min deposition which measured by α-step (Veeco; Dektak 8) as parameters of gas mixture at RF power in 50W and total gas pressure in 10 Pa. Film thickness tend to increase with increasing Ar gas mixture.

Table 2 Film thickness.

Gas mixture (O_2:Ar)	Film thickness (nm)
5:5	210
6:4	169
7:3	154
8:2	115
9:1	148

Figure 3 shows the surface morphology of the prepared film measured by AFM. The measurement was performed in non-contact AFM mode. The result suggested that the film is very smooth and mean roughness is ~nm. The films were found to be composed of small particles of 30~50 nm in diameter.

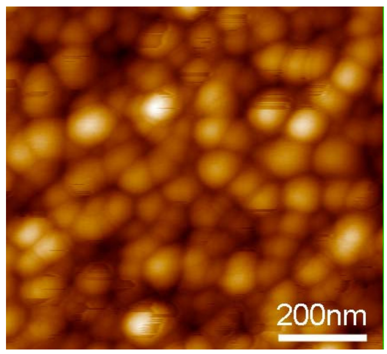


Fig. 3 Surface morphology of the prepared film. RF power:50W, P=50W, O_2: Ar =5:5.

Figure 4 shows XRD patterns of the WO_3 films deposited using the W target on the glass substrate. Substrate temperature was room temperature, and gas

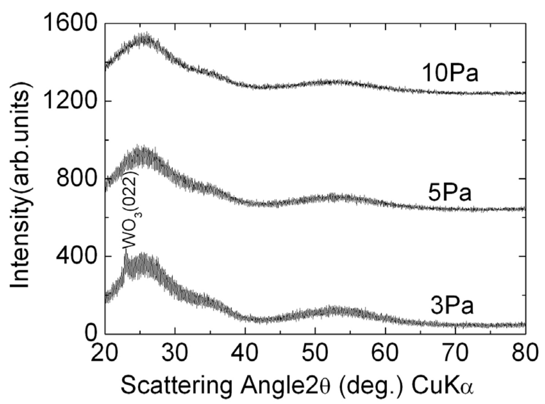


Fig. 4 XRD patterns of the WO_3 films deposited using the W target on the glass substrate. RF power:50W, O_2: Ar =5:5.

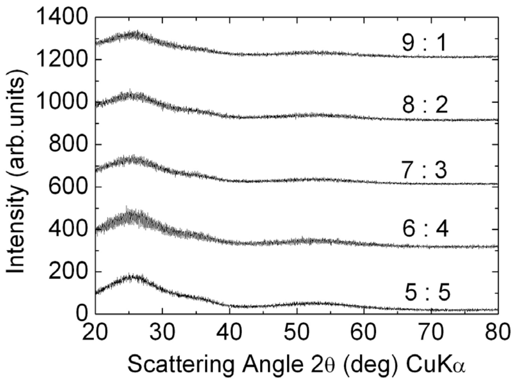


Fig. 5 XRD patterns of the WO_3 films deposited using the W target on the glass substrate. RF power:50W, P=10Pa, O_2: Ar =5:5~9:1.

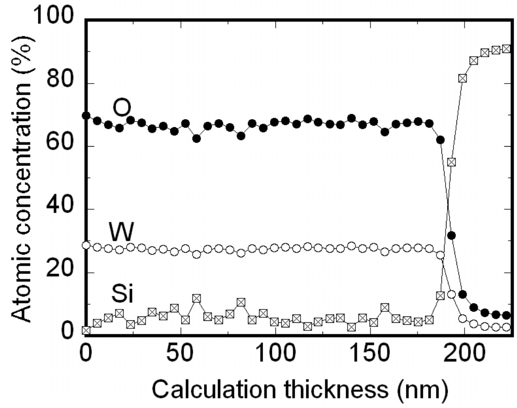
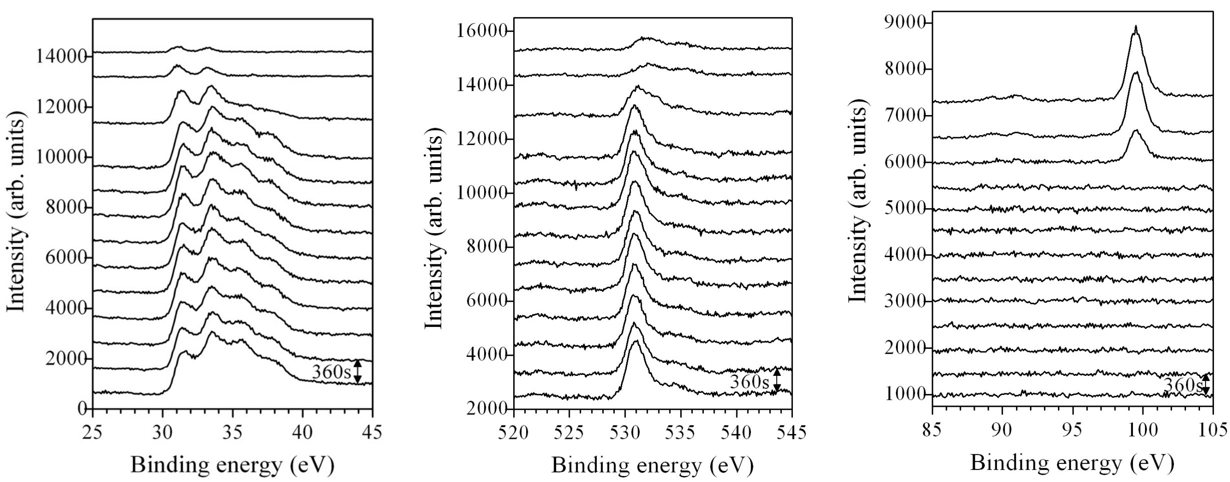


Fig. 7 Depth profile of the prepared WO_3 film estimated from Fig. 6. RF power:50W, P=10Pa, O_2: Ar =5:5.

mixture was O_2:Ar=5:5. At total gas pressure (P) was 3 Pa, a crystalline WO_3(022) peak can be observed. With increasing total gas pressure, the crystalline peaks disappear that means the films are amorphous. In general, the amorphous WO_3 thin film has a good performance as an electrochromic display. Figure 5 shows the XRD patterns of the WO_3 films deposited using the W target on the glass substrate as parameters of the O_2 and Ar gas mixture. There is no crystalline peak independent for the gas mixture in the Fig. 5. The results suggest that crystallinity of the film prepared at P = 10 Pa is amorphous independent for the gas mixture.

XPS analyses were carried out to determine the composition of the film and identify the valence states of the various species present therein. XPS spectra of W $4f_{5/2}$(33.8 eV, 37.9 eV), W $4f_{7/2}$(31.7 eV, 38.8 eV), O 1s(531.1 eV) and Si 2p peaks of the film prepared on the glass substrate are shown in Fig. 6. In this measurement, surface of the films were etched by Ar ion bombardment accelerated by 600 V. As ion bombardment time is 360s, each spectrum is the results after 360-4320 s etching. XPS spectra of W $4f_{5/2}$, W $4f_{7/2}$ and O 1s in the WO_3 film are shown in Figs. 6(a) and 6(b), respectively. The spectra show the presence of a symmetrical peak of W 4f incorporated with metal W (W $4f_{5/2}$(33.8 eV), W $4f_{7/2}$(31.7 eV)) and WO_3 (W $4f_{5/2}$(37.9 eV), W $4f_{7/2}$(38.8 eV), and O 1s incorporated with WO_x(O 1s(531.1 eV)).

Figure 7 show depth profile of the prepared WO_3 film estimated from etching rate of WO_3 bulk and Ar ion energy (600V). Estimated film thickness is about 195 nm which is almost same result of α-step measurement as shown in table 2 (210 nm). Fig 6 also shows that O/W composition ratio is 2.43. These results suggest that the amorphous type WO_x(x=2.43) film can be prepared under these conditions. The composition ratio of the prepared films can be controlled by gas pressure and Ar and O_2 gas



(a) W 4f (b) O 1s (c) Si 2p

Fig. 6 XPS spectra of the WO_3 films deposited using the W target on the glass substrate. RF power:50W, P=10Pa, O_2: Ar =5:5.

mixture, not shown here.

3.3 Electrochromic property

To study the electrochromic property, a DC voltage of 5 V was applied to the electrochromic display prepared using the WO_x film[12]. Figure 8 shows the visible light transmittance spectra of the film. Transmittance of the film increased from 380nm with wavelength and they are almost constant after 500nm. However, they decrease with increasing wavelength after applying a DC voltage. Transmittance spectrum of the film after applying voltage for vanishing shows almost the same as that before applying voltage. This tendency suggests that the film worked as electrochromic display and color changes from transparent to blue by applying a DC voltage.

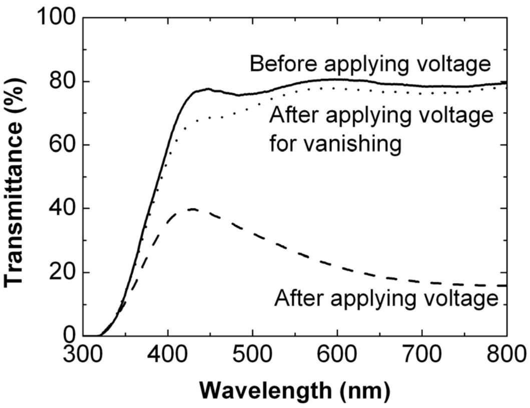


Fig. 8 Visible light transmittance spectrum of the film. RF power:50W, P=10Pa, O_2: Ar =5:5.

4. Conclusion

WO_x thin film was prepared on the ITO film coated flexible substrate using the RF magnetron sputtering method. Optical emission spectrum suggests mono-atomic neutral tungsten atoms presence in the RF plasmas but W ions, O neutrals atoms and molecular species cannot be detected in this condition. XRD results suggest that WO_x thin films at gas pressure of 10Pa are amorphous structure independent of a gas mixture. XPS analyses suggest that the amorphous type WOx(x=2.43) film can be prepared at the gas flow ratio of O_2:Ar=5:5, P =10Pa and RF power of 50W. Color of the prepared film change from transparent to blue after applying a DC voltage, which means that the prepared film under the condition worked as electrochromic display.

5. Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research in Priority Areas (B) (No.20340164). The authors wish to thank Prof. H. Fujiyama of Nagasaki University.

5. References

[1] P. R. Bueno, R. C. Faria, C. O. Avellaneda, E. R. Leite, L. O. S. Bulhoes, Solid State Ionics **158** 415 (2003).
[2] E. Masetti, M.L. Grilli, G. Dautzenberg, G. acrelli, M. Adamik, Sol. Ener. Mater. Sol. Cells **56** 259 (1999).
[3] X.G. Wang, Y.S. Jang, N.H. Yang, Y.M. Wang, L.Yuan, S.J. Pang, Sol. Ener. Mater. Sol. Cells **63** 197 (2000).
[4] K. Aguir, C. Lemire, D.B.B. Lollman, Sensor Actuators B **84** 1 (2002).
[5] T. Oyabu, J. Appl. Phys. **53** 2785 (1982).
[6] Y. Nagasawa, K. Tabata, H. Ohnishi, Appl. Suffice Sci. **121/122** 327 (1997).
[7] T. Brousse, D.M. Schleich, Sens. Actuators B **31** 77 (1996).
[8] S.S. Park, J.D. Mackenzie, Thin Solid Films **258** 268 (1995).
[9] K.H. Kim, T.S. Park, J. Kor. Phys. Soc. **18** 12 (1985).
[10] J.-I. Yang, H. Lim, S.-D. Han, Sens. Actuators B **60** 71 (1999).
[11] C. Cal, R. Macaluso, M. Mosca, Spectrochim Acta Part B **56** 743 (2001).
[12] Y. Suda, H. Kawasaki, T. Ohshima, Y. Yagyu, Thin Solid Films **516** 4397 (2008).
[13] H. Kawasaki, T. Ueda, Y. Suda, T. Ohshima, Sensors and Actuators B: Chemical **100** 266 (2004).
[14] T. Ohshima, Y. Yagyu, H. Kawasaki, Y. Suda, Transactions of the Materials Research Society of Japan **32** 175 (2007).