Oxygen partial pressure effects on the magnetron sputtered WO$_3$ films

G Merhan Muğlu$^{1}$, E Gür$^{1}$

$^1$Department of Physics, Faculty of Science, Atatürk University, 25240, Erzurum, Turkey.

E-mail: emregur@atauni.edu.tr

Abstract. Electrochromism is changing color of a substance in response to the applied an external electric field and the phenomenon is reversible. WO$_3$ is very attractive material due to its electrochromic properties as well as it is also attractive for many different applications such as gas sensors, phosphorous screen, textile, glass industry. In this study, it is aimed to provide optimization of the optical and structural characteristics of WO$_3$ by changing the growth parameters mainly the oxygen partial pressure. The partial pressure of oxygen was changed with increments of 0.7 mTorr. For the analysis, X-ray Diffraction (XRD), absorption, Raman spectroscopy measurements were used. When O$_2$ gas increased, peaks belong to the WO$_3$ was observed in XRD patterns at the 2 theta angles of 23.0, 11.0, 23.5 and 28.5 angles corresponding to the (002), (020) and (220) planes, respectively. This shows that there is a significant effect of increasing O$_2$ partial pressure in the formation of WO$_3$ films. The bandgap energy of the WO$_3$ thin films are found to be around 3.0 eV. Raman measurements showed vibrational modes of W-O-W stretching and bending modes which shows small shifts depending on the partial pressures of the O$_2$. Obtained results indicated that better crystal structure is obtained with higher O$_2$ gas partial pressure.

1. Introduction
Tungsten trioxide thin films have been extensively studied because of their potential application in electrochromic devices. The optical properties of these films can be changed in a reversible and persistent way under the influence of an applied voltage [1]. Electrochromism refers to the reversible change of color of thin films due to a small change in the voltage. This is important for smart windows and display applications [2-4]. It is widely accepted that the electrochromic process involves the simultaneous injection (or extraction) of electrons and charge compensating ions into interstitial sites of the WO$_3$ matrix [5]. For the polycrystalline films, the injected electrons behave as free-carriers leading to an increase in the near infrared reflectivity [6]. Nevertheless, scattering of the excess free electrons by extended defects, leads to lower reflectivity in this region [7].

Various methods have been used to prepare WO$_3$ thin films, including thermal evaporation [8,10,13,14], chemical vapor deposition (CVD) [12,15], sputtering [9,11,16,17,18,19] and pulsed laser deposition (PLD) [20,21]. In this study WO$_3$ thin film were deposited on the glass substrate by R.F magnetron sputtering a 99.9% pure tungsten target.
2. Experimental

RF magnetron sputtering has advantageous of having high deposition rates, sputtering of insulating targets, low power and low pressure operation conditions. WO$_3$ thin films were deposited on the Si (111), Si(100), ITO substrates by R.F. magnetron sputtering using a 99.9% pure 2'' diameter W target reactively. The vacuum chamber was evacuated to $5 \times 10^{-7}$ Torr base pressure before the deposition. Both argon and oxygen flows were controlled by mass flow controllers. The total pressure in the deposition chamber was kept constant at 12-15 mTorr. It was aimed to provide optimization of the optical and structural characteristics of WO$_3$ by changing the growth parameters mainly the oxygen partial pressure. The partial pressure of oxygen was changed with increments of 0.7 mTorr. While the applied power to the target was kept constant at 100 W and the substrate temperature was maintained at 350K.

Initially the deposition parameters were optimized to obtained WO$_3$ films with high transparency. Later, all the parameters except the deposition time were kept constant. The deposition parameters are listed in Table 1.

Table 1. R.F. sputtered parameters used for deposition of WO$_3$ thin films.

| Growth material | Base Pressure (torr) | Growth Pressure (mTorr) | Temperature (Celcius) | Gas1 Ar (sccm) | Gas2 O$_2$ (sccm) | Growth Rate ($\text{A}^\circ$/s) | Growth Time | Substrate |
|-----------------|----------------------|-------------------------|-----------------------|----------------|------------------|--------------------------|-------------|-----------|
| WO$_3$          | $1.5 \times 10^{-6}$ | 15.70                   | 330                   | 12.5           | 0.5              | 1.5                      | 130         | Si (111)  |
|                 |                      |                         |                       |                |                  |                          |             | Si (100)  |
|                 |                      |                         |                       |                |                  |                          |             | ITO glass |
| WO$_3$          | $6 \times 10^{-7}$   | 18.35                   | 311                   | 12.5           | 1.5              | 0.2                      | -           | Si (111)  |
|                 |                      |                         |                       |                |                  |                          |             | Si (100)  |
|                 |                      |                         |                       |                |                  |                          |             | ITO glass |
| WO$_3$          | $1.3 \times 10^{-6}$ | 18.88                   | 300                   | 12.5           | 1                | 0.6                      | 54          | Si (111)  |
|                 |                      |                         |                       |                |                  |                          |             | Si (100)  |
|                 |                      |                         |                       |                |                  |                          |             | ITO glass |
| WO$_3$          | $7.8 \times 10^{-7}$ | 20.3                    | 300                   | 12.5           | 2                | 0.1                      | 60          | Si (111)  |
|                 |                      |                         |                       |                |                  |                          |             | Si (100)  |
|                 |                      |                         |                       |                |                  |                          |             | ITO glass |

3. Results and Discussion

Increasing O$_2$ partial pressure led to the formation of XRD peaks for WO$_3$ films grown on ITO and the p-Si substrate. No XRD peak was observed for the thin films grown at the lowest oxygen partial pressure. XRD Peaks belong to the WO$_3$ films was observed at 23.0, 11.0, 23.5 and 28.5 angles corresponding to the (002), (020) and (220) planes, respectively. The peak intensity ratio of the of (002) plane to the other planes in films grown on the ITO substrate significantly has increased with increasing O$_2$ partial pressure. This shows that there is a significant effect of increasing O$_2$ partial pressure in the formation of WO$_3$ films. XRD results suggests that better crystal structure is possible by increasing O$_2$ partial pressure in WO$_3$ thin films.
Figure 1. XRD pattern of WO$_3$ thin films grown as depending on O$_2$ partial pressure.

Absorption plot of films that is grown at the highest O$_2$ partial pressure from the grown WO$_3$ thin films is shown in Fig.2. Starting around 400 nm, absorption spectra increases corresponding to the near band edge absorption of the grown WO$_3$ thin films. In the figure above, absorption spectrum of the pure glass substrates has shown in the plot which is used as the reference [20]. Very sharp absorption band edges of the sputtered WO$_3$ thin films suggest the successful high quality of the grown thin films.
Figure 3. The absorbance spectra were used to determine optical band gap energies of WO$_3$ on glass substrate.

Bandgap of the WO$_3$ thin films is shown in Fig. 3 by using the following relation for near band edge optical absorption of semiconductors,

$$\alpha = \left( \frac{K}{h} \right) (h\nu - E_g)^n$$  \hspace{1cm} (1)

where $\alpha$ is absorption co-efficient, $h\nu$ is the photon energy, $K$ is a constant, $E_g$ is the optical band gap and $n$ is a constant ($n$ equals 1/2 for allowed direct transitions) [25-29]. Fig. 3 shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for 4.45% O$_2$ partial pressure, 11.44% O$_2$ partial pressure, 13.79% O$_2$ partial pressure on glass substrate thin films; the linear portion of the curve is extrapolated to the energy (h\nu) axis and the intercept gives the value of optical band gap $E_g$ of the film [30]. The optical band gap values for 4.45% O$_2$ on glass substrate, 11.44% O$_2$, 13.79% O$_2$ thin films, determined from Fig. 3(a)-(c) as the 2.93 eV, 3.04 eV, 3.02 eV respectively.
Figure 4. Raman spectra of WO$_3$ thin films grown depending on to O$_2$ partial pressure.

The Raman spectroscopy is effective in revealing structural features and structural transitions in WO$_3$ owing to its high sensitivity to the small changes in the lattice positions of the tungsten atoms. The WO$_3$ exhibits the following sequence of crystal phases with increasing temperature: triclinic, monoclinic, orthorombic, tetragonal [21]; in particular, bulk WO$_3$ is monoclinic-$\gamma$ between 20°C and 330°C and it is orthorombic-$\beta$ between 330°C and 740°C [22]. When Raman spectrum of the as prepared WO$_3$ thin films are examined, it is seen four well defined peaks located at 807, 710, 327, and 267 cm$^{-1}$. The high-frequency peaks at 807 and 710 cm$^{-1}$ were attributed to the W–O–W stretching vibration mode, while the low frequency ones (i.e., 327 and 267 cm$^{-1}$) were attributed to the W–O–W bending mode. The peaks shown in the present study similar to those for monoclinic WO$_3$ thin films [23,24]. WO$_3$ thin films were
not shown for 0.7 mTorr. The details of the Raman peaks, wavenumbers and Full Width at Half Maximum (FWHM) obtained is given in table 1 and 2, respectively.

**Table 2.** Peak analysis of WO$_3$ thin films in Raman Spectroscopy

| Si n-tipi | % 4.45 O$_2$ (0.5 sccm) | % 7.41 O$_2$ (1 sccm) | % 11.44 O$_2$ (1.5 sccm) | % 13.79 O$_2$ (2 sccm) |
|-----------|-------------------------|------------------------|--------------------------|------------------------|
| 1) (w-O-W) stretching mode | - | 804,965 | 805,594 | 804,126 |
| 2) (w-o-W) stretching mode | - | 711,399 | 714,545 | 708,881 |
| 3) (W-O-W) bending mode | - | 300,42 | 300 | 300,629 |
| 4) (W-O-W) Bending mode | - | 268,741 | 268,741 | 265,385 |

| Si p-tipi | % 4.45 O$_2$ (0.5 sccm) | % 7.41 O$_2$ (1 sccm) | % 11.44 O$_2$ (1.5 sccm) | % 13.79 O$_2$ (2 sccm) |
|-----------|-------------------------|------------------------|--------------------------|------------------------|
| 1) (W-O-W) stretching mode | - | 805,385 | 805,594 | 805,385 |
| 2) (W-O-W) stretching mode | - | 714,755 | 714,126 | 712,238 |
| 3) (W-O-W) bending mode | - | 299,79 | 300,839 | 301,259 |
| 4) (W-O-W) bending mode | - | 267,902 | 268,112 | 267,692 |

**Table 3.** FWHM of WO$_3$ thin films in Raman Spectroscopy

| Si n-tipi | % 4.45 O$_2$ (0.5 sccm) | % 7.41 O$_2$ (1 sccm) | % 11.44 O$_2$ (1.5 sccm) | % 13.79 O$_2$ (2 sccm) |
|-----------|-------------------------|------------------------|--------------------------|------------------------|
| (W-O-W) stretching mode | - | 24,71823 | 23,5692 | 30,94485 |
| (W-O-W) stretching mode | - | 29,81282 | 24,4564 | 31,11964 |
| (W-O-W) bending mode | - | 4,80163 | 10,48127 | 7,70834 |
| (W-O-W) Bending mode | - | 9,73598 | 12,22645 | 17,08973 |

| Si p-tipi | % 4.45 O$_2$ (0.5 sccm) | % 7.41 O$_2$ (1 sccm) | % 11.44 O$_2$ (1.5 sccm) | % 13.79 O$_2$ (2 sccm) |
|-----------|-------------------------|------------------------|--------------------------|------------------------|
| (W-O-W) stretching mode | - | 24,70637 | 23,60933 | 26,19571 |
| (W-O-W) stretching mode | - | 17,0363 | 21,83434 | 19,42854 |
| (W-O-W) bending mode | - | 5,78893 | 7,22312 | 9,74574 |
| (W-O-W) Bending mode | - | 14,24921 | 9,9938 | 13,97798 |
Figure 5. FWHM of WO3 thin films in Raman Spectroscopy for n and p type Si

4. Conclusion
To summarize, in the present study, the structural, optical properties and the electrochromic characteristics of oxygen sputtered WO3 films have been investigated. WO3 thin films were not shown 4.45% O2 peaks whereas the best peaks were shown 11.44% O2. Tungsten oxide is one of the most promising inorganic materials which exhibit excellent electrochromic, photochromic and gasochromic properties and it has been widely investigated to be used in electrochromic, gasochromic, solar energy, optical modulation, writing–reading–erasing optical devices.

References
[1] Regragui M, Jousseaume V, Addou M, Outzourhit A, Bernede J C and El-Idrissi B 2001 Thin Solid Films 397 238–243
[2] Roth S, Ignatowitz M, Muller P, Monch W and Oesterschulze E, 2011 Microelectronics J. 88 2349–2351
[3] Granqvist C G 2012 Sol. Energy Mater. Sol. Cells 99 1–13.
[4] Mihelec’ic’ M, Jerman I and Orel B 2013 Prog. Org. Coat. 76 1752–1755.
[5] Dautremont-Smith W C 1982 Displays 3 pp 67-80.
[6] Goldner R B, Chapman R L, Foley G, Goldner E L, Haas T, Norton P, Seward G and Wong K K 1986 Sol. Energy Mater. 14 195.
[7] Goldner R B, Brofos A, Foley G, Goldner E L, Haas T E, Henderson W, Norton P, Ratnam B A, Weis N and Wong K K 1984 SPIE Proc. 502 54.
[8] Brezesinski T, Fattakhova-Rohlfing D, Sallard S, Antonietti M, and Smarsly B M 2006 Small 2(10), 1203
[9] Berveglieri G, Depero L, Groppelli S, and Nelli P 1995 Sens. Actuators, B 1 26(1–3), 89.
[10] Cantalini C, Sun H T, Faccio M, Pelino M, Santucci S, Lozzi L, and Passacantando M 1996 Sens. Actuators, B 31(1–2), 81
[11] Di Giulio M, Manno D, Micocci G, Serra A, and Tepore A 1997 J. Phys. D: Appl. Phys. 30(23), 3211
[12] Tong M, Dai G, Wu Y, He X, Gao D and Mater J 2001 Sci. 36(10), 2535
[13] Agrawal A and Habibi H 1989, Thin Solid Films 169(2), 257.
[14] LeGore L J Greenwood, O D Paulus, Frankel D J, Lad R J, Vac J 1997 Sci. Technol, A 15(3), 1223.
[15] Tagtstrom P and Jansson U 1999 Thin Solid Films 352(1–2), 107.
[16] Akram H, Tatsuoka H, Kitao M, and Yamada S 1987 J. Appl. Phys. 62(5), 2039.
[17] Kaneko H, Nishimoto S, Miyake S K, and Suedomi N 1986 J. Appl. Phys. 59(7), 2526.
[17] Kobayashi Y, Terada S, and Kubota K 1989 Thin Solid Films **168**(1), 133.
[18] Li M, Altman E I, Posadas A, and Ahn C H 2004 Thin Solid Films **446**(2), 238.
[19] Garg A, Leake J A and Barbe Z H 2000 J. Phys. D: **Appl. Phys.** **33**(9), 1048.
[20] Wang C, Sahu D R, Wang S, Chung-Kwei C and Huang J 2012 *J. Phys. D: Appl. Phys.* **45**, 225-303.
[21] Lu D Y, Chen J, Chen H J, Gong L, Deng S Z, Xu N S 2007 *Appl. Phys. Lett.* **90**, 041919
[22] Cazzanelli E, Vinegoni C, Mariotto G, Kuzmin A, Purans J 1999 *Sol. St. Ionics* **123**, 67
[23] Zhou L, Ren Q J, Zhou X F, Tang J W, Chen Z H and Yu C Z 2008 *Microporous Mesoporous Mater* **109**, 248–257.
[24] Siciliano T, Tepore A, Micocci G, Serra A, Manno D and Filippo E 2008 *Sens. Actuators, B* **133**, 321–326.
[25] Hamberg L 1984 Indium tin oxide thin films: basic optical properties and applications to energy efficient windows, *Ph.D. Thesis, Chalmers University of Technology*, Gothenburg, Sweden.
[26] Born M, Wolf E 1983 *Principles of Optics* (Oxford: Pergamon Press)
[27] Heavens O S, 1970 *Optical Properties of Thin Films*, Dover, New York; Heavens O.S. 1965 *Thin Film Physics*, Methuen, London.
[28] Pankove J I, 1971 Optical Processes in Semiconductors, *Prentice-Hall, Englewood Cliffs*, N.J.
[29] Ozer N, Tepehan F, Tepehan G 1997 *Proc. SPIE—Int. Soc. Opt. Eng. (USA)* **3138**, 9–31.
[30] Miller E L, Paluselli D, Marsen B, Rocheleau R E 2004 *Thin solid Films* **466**, 307.