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On the Bonding and Electrochemical Performance of Sputter Deposited WO$_3$ Thin Films

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Abstract. Tungsten oxide (WO$_3$) thin films have attained a distinct and special place in the field of electrochromism. Therefore, any sort of study towards this material will invariably has lot of importance and technological significance. The films of WO$_3$ were deposited by reactive magnetron sputtering at various partial pressures and annealed at 475$^\circ$C. There is a tremendous change in the bonding characteristics, which eventually show significant change in the optical and electrochemical behavior. The bandgap of WO$_3$ films is found to be increasing with different oxygen partial pressure. A systematic study of cyclic voltammetry has been done to analyze the electrochemical behavior of WO$_3$ films. Oxidation and reduction peak currents have shown an increasing trend with the oxygen partial pressure. Raman spectroscopy has revealed the improvement in the atomic ordering in WO$_3$ films.

1. Introduction

Tungsten oxide (WO$_3$) thin films acquired great technological significance due to its best electrochromic performance[1].

WO$_3$ is n-type semiconductor, which has colour memory and shows high coloration efficiency. In the oxidized state it is in W6+ state appearing colour less, and converts to deep blue colour in reduced state i.e W5+ state. Briefly, when metal ions M$^+$ (M = H, Li, Na, or K) intercalate into the WO$_3$ lattice structure the colour of the film changes to dark blue. While de-intercalating of these metal ions from the WO$_3$ lattice, the film turns out to transparent or colour less. The general equation which explains this is as follows.

$$\text{WO}_3 + xM^+ + xe^- \rightarrow M_x \text{WO}_3$$

Thus, the optical property of WO$_3$ films transforms from transparent to an absorbing nature due to the filling of t2g band of perovskite structure by the excess electrons [2].

There are different models to explain the coloured and bleached behaviour of these films. One such model says, a polaron [3] for which electrons got trapped at tungsten sites when injected into WO$_3$ lattice to form W5$^+$ centres. A small polaron would be formed from the perturbation of surrounding lattice. It is also evident that there will be an optical transfer of the polaron from a W5$^+$ site to a close
by W6+ site. Poly crystalline or crystalline samples have got another model to explain the electrochromic behaviour [4, 5]. The conduction there is explained by a free electron model of Drude type. Furthermore, it is not obvious whether a unified description can be applied to the large variety of materials produced by methods as different as thermal evaporation, radiofrequency reactive sputtering, anodic oxidation, etc.

Different methods are used to prepare WO$_3$ films such as thermal evaporation [6], anodic oxidation [7], spray pyrolysis [8], sol-gel [9], and molecular beam deposition [6] and sputtering [10]. Among these, sputtering has the advantage of getting highly dense films, high directional deposition and smooth films also large area deposition [11]. The physical properties of the magnetron sputtered films mainly depend on the deposition parameters such as oxygen partial pressure, substrate temperature, and sputter power. In the present investigation, thin films of WO$_3$ were deposited by RF magnetron sputtering of metallic tungsten target under various oxygen partial pressures. The influence of oxygen partial pressure on the structural, surface morphology, optical properties and electrochemical properties was systematically studied and the results were reported.

## 2. Experimental details

The WO$_3$ thin films were deposited on Corning glass and FTO coated glass substrates. Corning glass and FTO coated glass substrates cleaned ultrasonically using soap solution followed by DI water and rinse and finally dried using nitrogen gas. Before deposition again cleaned with acetone and placed in vacuum chamber. Vacuum sputtering chamber with an ultimate low pressure of 1.0× 10$^{-6}$mbar is achieved using 1000LPS Turbo molecular pump backed by a1000 LPM rotary pump. Tungsten-trioxide thin films are prepared using high pure tungsten target of 3 inch diameter and 3mm thick was sputtered in Oxygen (O)-Argon (Ar) ambient atmosphere. Substrates were kept at a distance of9 cm from the target during the deposition. Before every deposition, pre-sputtering was performed in Argon environment for 15 min to remove the adsorbed contaminants and the native oxide from the surface of the tungsten target. The films were prepared on the substrates held at room temperature at different oxygen partial pressures in the ranges 2×10$^{-4}$ to 1×10$^{-3}$mbar. The RF power fed to the sputter target was 40W using RF power source. Deposition conditions maintained during the preparation of WO$_3$ films are given in Table 1.

| Sputter target | Tungsten (3 inch dia.) |
|----------------|-----------------------|
| **Substrates** | Corning and FTO coated glass |
| **Base pressure** | 1×10$^{-6}$ mbar |
| **Target to substrate distance** | 9 cm |
| **Oxygen partial pressure (pO2)** | 2×10$^{-4}$, 4×10$^{-4}$, 6×10$^{-4}$, 8×10$^{-4}$ and 1×10$^{-3}$ mbar |
| **Argon flow rate** | 25 sccm |
| **Working Pressure** | 1×10$^{-2}$ mbar |
| **RF power** | 40W |
| **Deposition temperature** | Room temperature |
| **Post annealing temperature** | 475°C (2hrs) |
3. Results and discussion

3.1 Raman spectroscopy: Figure 1 shows the Raman spectrum of films deposited at various partial pressures.

![Raman spectra of WO₃ films deposited at various oxygen partial pressures.](image)

**Figure 1.** Raman spectra of WO₃ films deposited at various oxygen partial pressures.

From the figure it is evident that with the oxygen partial pressure there is an improvement in the sharpness of the characteristic peaks, which infers increase in the atomic ordering in the WO₃ lattice.

3.2 Optical properties: Figure 2 shows the optical transmittance of the films deposited at various partial pressures. From the figure it is evident that, the transparency has been increasing with the partial pressure.

![Optical transmittance plots of WO₃ films deposited at various oxygen partial pressures.](image)

**Figure 2.** Transmittance plots of WO₃ films deposited at various oxygen partial pressures.
Optical absorption coefficient ($\alpha$) of prepared thin films are found using below equation

$$\alpha h\nu = (h\nu - E_g)^n$$

$n=1/2$ for direct allowed transitions and 2 for indirect transitions, ‘$\alpha$’ is the absorption coefficient, ‘$E_g$’ is optical bandgap and ‘$h\nu$’ is the incident photon energy. From the Tauc-plots with $n=1/2$, we found the variation in the optical bandgap of WO$_3$ films by taking a straight line fit of $(\alpha h\nu)^{2}$ on to the energy axis. Figure 3 shows the WO$_3$ bandgap variation with different oxygen partial pressures.

![Figure 3. Bandgap variation in WO$_3$ films deposited at various oxygen partial pressures.](image)

Figure 4 shows the typical morphology and cross-section of WO$_3$ films, which shows that the films are having grains.

![Figure 4. Typical surface morphology (a) and cross sectional (b) of WO$_3$ films](image)

### 3.3 Cyclic Voltammetry:

Figure 5 to Figure 9 shows the cyclic voltammetry (CV) plots of WO$_3$ films deposited at various oxygen partial pressures. Each figure in turn shows the variation in the CV characteristics at various scan rates.
Figure 5. CV plots of WO$_3$ films deposited at pO$_2=2\times10^{-4}$ mbar.

Figure 6. CV plots at different scan rates of WO$_3$ films deposited at pO$_2=4\times10^{-4}$ mbar.
Figure 7. CV plots at different scan rates of WO$_3$ films deposited at pO$_2$ = 6x10$^{-4}$ mbar.

Figure 8. CV plots at different scan rates of WO$_3$ films deposited at pO$_2$ = 8x10$^{-4}$ mbar.
Figure 9. CV plots at different scan rates of WO$_3$ films deposited at pO$_2$=1x10$^{-3}$ mbar.

The peak current values during oxidation and reduction of these WO$_3$ films during CV measurements is shown in Figure 10.

Figure 10. Peak current plots during oxidation and reduction of WO$_3$ films deposited at various oxygen partial pressures.
4. Conclusion:

Tungsten oxide (WO$_3$) thin films have been deposited at various partial pressures and annealed at 475$^\circ$C. Raman spectroscopy, UV-visible spectroscopy, cyclic voltammetry has been performed. Bandgap of the films was found to be increasing with the oxygen partial pressure. From Raman spectroscopy it is found that there is a tremendous change in the atomic ordering of WO$_3$ films, which eventually show a significant change in the optical and electrochemical behavior. A systematic study of cyclic voltametry has been done to analyze the electrochemical behavior of WO$_3$ films. Oxidation and reduction peak currents have shown an increasing trend with the oxygen partial pressure.

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