

Thickness-dependent Electrochromic Properties of Amorphous Tungsten Trioxide Thin Films

K.J. Patel^{1,*}, G.G. Bhatt¹, S.S. Patel², R.R. Desai², J.R. Ray³, C.J. Panchal^{4,†}, Priya Suryavanshi⁴,
V.A. Kheraj⁵, A.S. Opanasyuk⁶

¹ BITS Edu Campus, Varnama, Vadodara, Gujarat, India

² Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India

³ H. V. H. P. Institute of P.G. Studies and Research, Kadi Sarva Vishwavidyalaya, Kadi, Gujarat, India

⁴ The M. S. University of Baroda, Vadodara-390001, India

⁵ S. V. National Institute of Technology, Surat 395007, India

⁶ Sumy State University, 2, Rymtskyi-Korsakov Str., 40007 Sumy, Ukraine

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Tungsten Trioxide (WO₃) thin films were grown by thermal evaporation method to study the effect of film's thickness on its electrochromic (EC) properties. The WO₃ thin films of different thicknesses were grown on Indium Tin Oxide (ITO) coated glass and soda lime (bare) glass substrate held at room temperature. The surface composition of the thin films was investigated using X-ray photoelectron spectroscopy measurement, which showed the oxygen to tungsten atomic composition ratio to be nearly 2.97. The EC properties of the thin films were examined using electrochemical techniques. Cyclic-voltammetry shows the diffusion coefficient (*D*) of the intercalated H⁺ ion in the WO₃ thin film increases with the film's thickness. It turns out that the 'thicker' film exhibits better coloration efficiency (CE) as compared to the 'thinner' film. The coloration time was found to be independent of film thickness; however, the bleaching time increases as the film thickness increases.

Keywords: Electrochromic, Thermal evaporation, Tungsten trioxide.

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1. INTRODUCTION

Transition metal oxides are interesting from the perspective of technology. In particular, tungsten trioxide (WO₃) has generated considerable interest due to its enormous electrochromic (EC) properties [1, 2]. Electrochromism is the phenomenon in which alteration of color occurs by applying a voltage. WO₃ thin film can change color reversibly between deep blue and transparent by ion intercalation/de-intercalation. Amorphous WO₃ films are extensively used in EC application due to its excellent electrochromic properties compared to crystalline films [3, 4]. In the amorphous WO₃ thin films the absorption modulation during ion and electron insertion occurs due to electron exchange between adjacent W⁶⁺, W⁴⁺, and W⁵⁺; the inserted electrons are localized in W⁵⁺ sites and they polarize their surrounding lattice to form small polarons, which then absorb the incident photons [5]. Electrochromic WO₃ is one of the most promising materials for electrochromic devices due to its high electrochemical efficiency and versatility towards the application in opto-electronic devices. WO₃ thin-films are efficient for electrochromic applications such as smart-windows, electrochromic mirrors, and display devices etc [6, 7]. Optical modulation, coloration efficiency (CE), and switching time are important parameters for the device construction which was directly affected by film structure and thickness. Some applications do not require a rapid colour change such as for the EC windows, which require a very slow response; however, applications such as display devices, require a more rapid response. In our previous study we have already observed that the

WO₃ films grown at room temperature (RT) are amorphous in nature [8]. The present work includes the effect of film's thickness on the various electrochemical parameters viz. diffusion coefficient, transmission modulation, CE and switching time.

2. EXPERIMENTAL

The WO₃ thin films were grown at room temperature by thermal evaporation of WO₃ powder (Sigma Aldrich, 99.9%), on organically cleaned soda-lime glass substrate and on Indium Tin Oxide (ITO) coated glass substrate. The ITO thin films are deposited by RF magnetron sputtering onto the externally unheated soda-lime glass substrates having a sheet resistance of 5–10 ohm/□ [9]. The WO₃ films were grown at a base pressure of 10⁻⁵ mbar. WO₃ thin films of different thickness viz. 1000 Å, 2000 Å, and 3000 Å were deposited at a constant rate of 4 Å s⁻¹, which was monitored and controlled using thin-film deposition controller (Sigma Instruments, SQC 122c).

The surface composition of the thin films was investigated using X-ray photoelectron spectroscopy (XPS). The XPS measurement was carried out using VSW ESCA instrument, with Al-Kα (1486.6 eV) X-ray source at base vacuum of 8.0 × 10⁻¹⁰ Torr. The EC properties of the samples were examined using electrochemical cell, with WO₃ film deposited on ITO coated glass substrate acting as the working electrode, stainless steel plate was used as the counter electrode and 0.1M H₂SO₄ as an electrolyte for H⁺ ion intercalation. The electrochemical parameters viz. anodic peak current (*i_{pa}*), cathodic spike current (*i_{pc}*), and diffusion coefficient (*D*) of the H⁺ ion for intercalation/de-intercalation through the WO₃ thin film has

* keyur.tithal@gmail.com

† cjpanchal_msu@yahoo.com

been studied using cyclic-voltammetry (C-V). The variation of the optical density of the WO_3 thin films was measured by applying a constant current density 0.4 mA/cm^2 for 25 s, required to color and bleach the electrochromic thin film and concomitantly measuring the transmission spectra for both the fully color and the bleach states; this leads to the evaluation of the CE. The switching time of the WO_3 thin film was measured using the chronoamperometry technique, with concurrently measuring the optical transmittance between the colored and bleached states. The optical measurement was performed using the laser diode ($\lambda = 650 \text{ nm}$), a Si photo-detector, and the experimental setup was automated using LabVIEW (ver 8.2) program.

3. RESULTS AND DISCUSSION

3.1 Compositional Characterization

The compositional characterization of WO_3 thin films deposited on bare glass substrate held at RT was carried out using the XPS measurements.

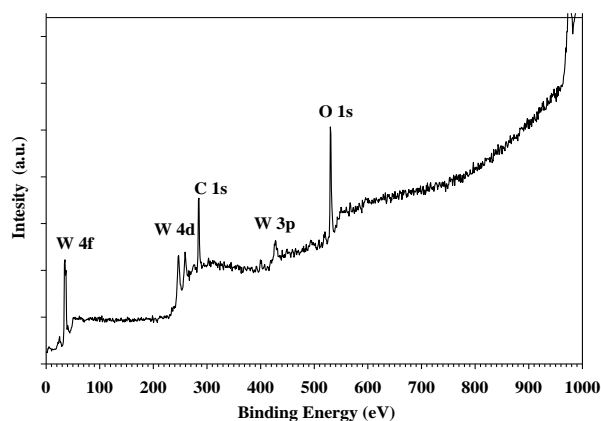


Fig. 1 – The XPS survey scan spectra of the RT deposited WO_3 thin films

Fig. 1 shows the survey scan spectrum of WO_3 thin film in the binding energy range 0 – 1000 eV. It was observed that, there was apparently no peak other than that of W and O with C as reference peak, which shows the purity of the WO_3 thin film's surface. Furthermore, to reveal the ratio of O to W, a detail scan spectra of was measure for W4f and O1s.

From Fig. 2(a), the XPS spectra of W4f doublet corresponding to $4f_{7/2}$ and $4f_{5/2}$ are at binding energy 34.65 and 36.78 eV, respectively. The XPS O1s peak (Fig. 2(b)) consists of two components: one at binding energy 530.6 eV, assigned to the oxygen in WO_3 films and a smaller one at 232.5 eV assigned to water molecules adsorbed on the film's surface [10]. Therefore, for the composition measurement on WO_3 films only lower binding energy peak is used. The atomic concentration of O1s and W4f are 74.82 and 25.18 % respectively, and the oxygen to tungsten ratios (O/W), which is estimated from the atomic concentration of O1s and W4f, is 2.97.

3.2 Electrochromic Characterization

Diffusion Coefficients (D) Measurement

The Diffusion coefficient of the WO_3 films was

measured by the C-V measurements. Fig. 3 shows a typical voltammogram for WO_3 thin films deposited on ITO coated glass substrate held at RT. The C-V was performed at a scan rate of 100 mV/s in $0.1\text{M H}_2\text{SO}_4$ solution in voltage range -1.5 to $+1.5$ volt. During the negative potential cycle, cathodic spike (i_{pc}) is observed with films being dark blue, and for the positive potential cycle an anodic peak (i_{pa}) is observed, with films being colorless, which was used to further calculate the diffusion coefficient, D . The magnitude of the both, the cathodic spike current and anodic peak current, increases with the film's thickness.

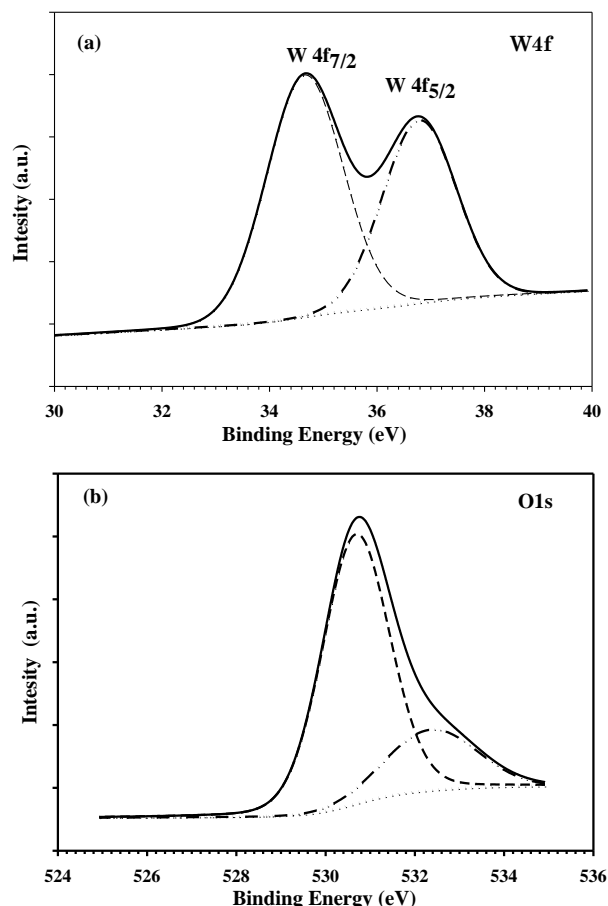


Fig. 2 – The (a) W4f and (b) O1s XPS spectra for the RT deposited WO_3 thin film

The D of the H^+ ion in the WO_3 thin film have been calculated by the Randles–Servcik equation, which was given by [11],

$$i_p = 2.72 \times 10^5 \times n^{\frac{3}{2}} \times D^{\frac{1}{2}} \times C_0 \times v^{\frac{1}{2}} \quad (1)$$

where, D is the diffusion coefficient in cm^2s^{-1} , C_0 is the concentration of active ions in the electrolyte solution in mol cm^{-3} , v is the potential scan-rate mV/s , i_p is the peak current density in A cm^{-2} from cyclic voltammogram, and n is the number of electrons, which is assumed to be unity. The electrochemical parameters like the anodic peak current, cathodic spike current, and D are extracted from C-V measurements are shown in Table 1.

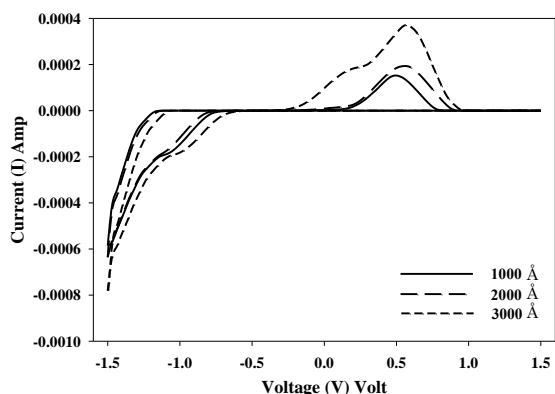


Fig. 3 – Cyclic voltammogram of a WO_3 thin film prepared at RT for different thickness

Table 1 – Electrochemical parameter of the WO_3 thin films grown at RT for intercalation of H^+ ions

Film Thickness (Å)	Anodic peak current (i_{pa}) (Amp)	Cathodic spike current (i_{pc}) (Amp)	Diffusion coefficient (D) ($\text{cm}^2 \text{s}^{-1}$)	
			For i_{pa}	For i_{pc}
1000	1.51×10^{-4}	5.85×10^{-4}	4.78×10^{-10}	7.17×10^{-9}
2000	1.93×10^{-4}	6.35×10^{-4}	8.60×10^{-10}	9.32×10^{-9}
3000	3.71×10^{-4}	7.81×10^{-4}	3.84×10^{-10}	1.70×10^{-9}

The D of the H^+ ions in WO_3 thin film are maximum for 3000 Å film thicknesses. As the thickness of the films decreases, the D decreases so number of ions intercalated /de-intercalated in the films is decreases.

Coloration Efficiency Measurement

The CE was measured using constant current measurement. The CE is one of the important parameters for the device construction. It is defined as the change in the optical density (ΔOD) per unit injected/extracted of charge (q) per unit electrode area (A) at a certain wavelength, i.e.

$$\text{CE}(\lambda) = \frac{\Delta\text{OD}(\lambda)}{Q} = \frac{\log(T_b/T_c)}{q/A} \quad (2)$$

where, ΔOD is the change in the optical density and Q (mC cm^{-2}) is the charge injected per unit electrode area of the thin films and T_b and T_c are the transmittance in the bleach and the colored state, respectively.

The variation of the optical density of the WO_3 thin films was measured by applying a constant current density 0.4 mA/cm^2 for 25 s, required to color and bleach the electrochromic thin films. Typical optical transmittance spectra of all samples measured for colored and bleached states are shown in Fig. 4.

For comparison, the CE and the transmittance modulation at 650 nm and 1000 nm wavelength are summarized in Table 2. The CE of the WO_3 thin films improved with the film's thickness.

The films with 3000 Å thickness shows the CE of $90 \text{ cm}^2/\text{C}$. The improvement in the CE is caused by the more number of ions intercalated/de-intercalated with film's thickness.

Switching Time Measurement

The response time performance of WO_3 thin films

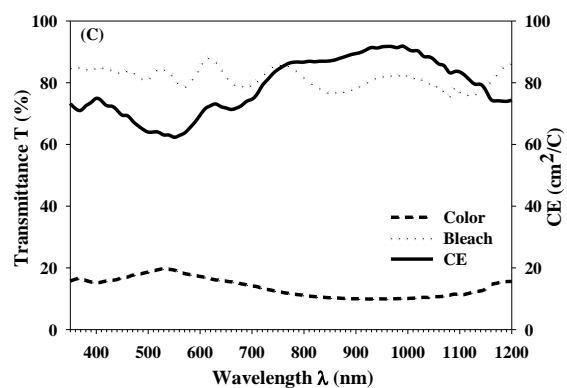
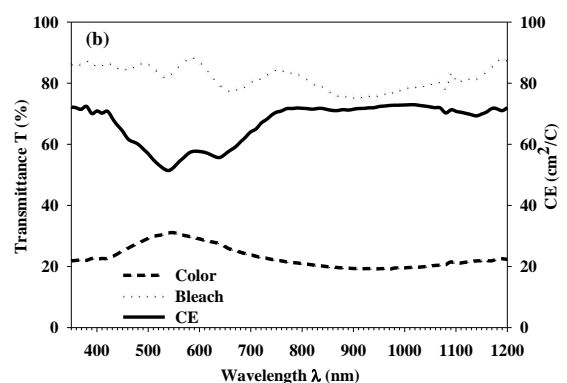
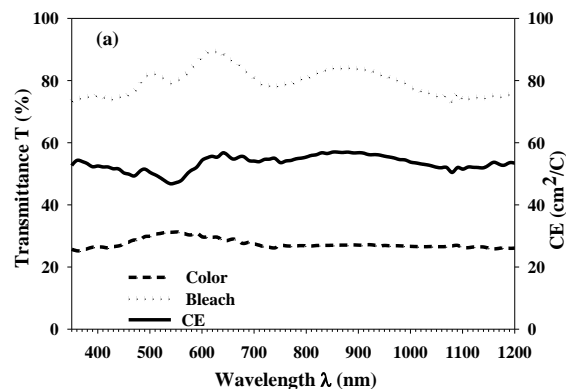


Fig. 4 – The transmittance spectra in the color and bleach state and CE of RT grown WO_3 thin film of thickness (a) 1000 Å, (b) 2000 Å and (c) 3000 Å

Table 2 – The transmittance modulation and CE for RT grown WO_3 thin film of different film thickness

Film Thickness (Å)	Transmittance Modulation (ΔT) %		Coloration Efficiency (CE) cm^2/C	
	$\lambda = 650 \text{ nm}$	$\lambda = 1000 \text{ nm}$	$\lambda = 650 \text{ nm}$	$\lambda = 1000 \text{ nm}$
1000	58	51	55.84	53.74
2000	52	59	56.77	72.86
3000	66	72	71.79	90.90

were characterized using chronoamperometry technique with concurrently optical data recorded between color and bleach state. Chronoamperometry measurements were made by applying a square-wave potential of $\pm 1.5 \text{ V}$ at a frequency of 0.05 Hz to the electrochemical cell. The optical measurement was performed with the help of a laser diode ($\lambda = 650 \text{ nm}$)

and an Si photo-detector, and the entire experiment was automated using LabVIEW (ver 8.2) program. Fig. 5 shows the current and transmittance variation versus time, at 650 nm wavelengths on application of a square-wave potential of ± 1.5 V at a frequency of 0.05 Hz.

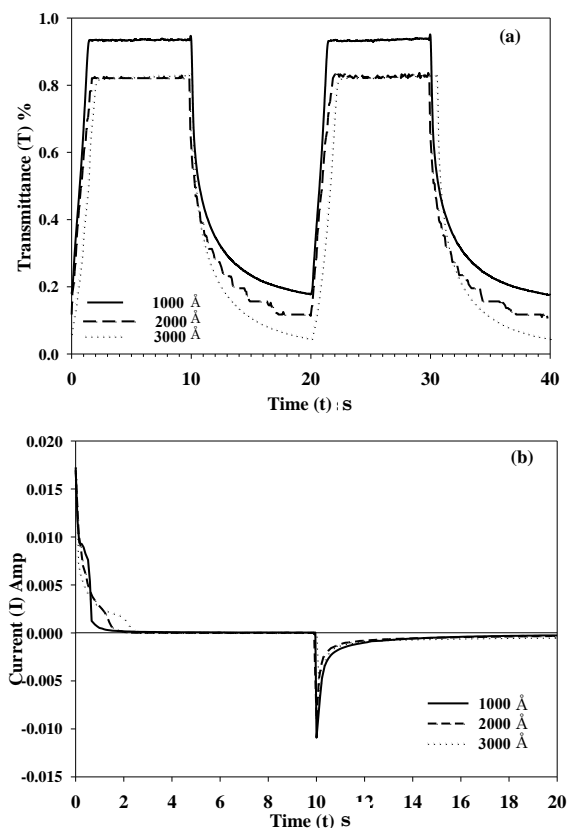


Fig. 5 – (a) The optical transmittance variation at 650 nm and (b) the current of the WO_3 thin films grown at RT with different thickness

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The switching times of WO_3 thin films are estimated from the optical modulation and current as function of time. The switching time data are summarized in Table 3.

Table 3 – Switching time data at 650 nm wavelength for different thickness of WO_3 thin films

Film Thickness (\AA)	Bleaching time (t_b) s	Coloration time (t_c) s
1000	1.4	10
2000	1.7	10
3000	2.5	10

From the switching time measurements, we observe that the bleaching current decreases sharply to zero while coloration current decreases relatively slowly indicating that the bleaching is much faster than coloration. In colored state WO_3 films are highly conductive and in bleach state the films are insulating indicating that the conductor to insulating transition is much faster than the insulating to conductive transition. In bleaching time measurement, the thinner film exhibit faster switching as compared to the thicker films and minimum bleaching time of 1.4 s was observed for 1000 \AA film thickness. In case of the coloration, all films take about the same coloration time ~ 10 s.

4. CONCLUSIONS

The WO_3 thin films of different thicknesses were grown by the thermal evaporation for substrates at RT. The EC properties of WO_3 thin films grown at RT are influence by the film thickness. The XPS analysis shows that the oxygen to tungsten atomic composition ratio (O/W) for the RT grown films was nearly 2.97. The diffusion coefficient of the H^+ ions in WO_3 thin films increases with the film's thickness, which shows that more number of H^+ ions are intercalated/de-intercalated in films, which improves the CE of the thin film. The coloration time was found to be independent of film's thickness, however, the bleaching time increases as the film's thickness increases.