

Investigation of x-ray photoelectron spectroscopic (XPS), cyclic voltammetric analyses of WO₃ films and their electrochromic response in FTO/WO₃/electrolyte/FTO cells

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Abstract

Electrochromic thin films of tungsten oxide (WO₃) were prepared on transparent conducting oxide substrates, i.e., fluorine doped tin oxide coated (FTO or SnO₂:F) glass and microscopic glass substrates by the electron beam evaporation technique using pure WO₃ (99.99%) pellets at various substrate temperatures (i.e., T_{sub} = room temperature (RT, 30 °C), 100 °C and 200 °C). The films were prepared under vacuum of the order of 1×10^{-5} mbar. The room temperature prepared films were further post-heat-treated (T_{anne}) at 200 and 300 °C for about 1 h in the vacuum environment. The prepared films are in monoclinic phase. The chemical composition has been characterized by using the XPS technique. The W 4f and O 1s core levels of WO₃ films have been studied on the samples. The obtained core level binding energies revealed the WO₃ films contained six-valent tungsten (W⁶⁺). The electrochemical nature of the films was studied by a three-electrode electrochemical cell in the configuration of FTO/WO₃/H₂SO₄/Pt, SCE, using the cyclic voltammetry (CV) technique. Electrochromic devices (ECDs) of the general type FTO/WO₃/electrolyte/FTO were studied. The films produced at higher substrate temperature show smaller modulation of the visible spectrum, compared with the films produced at lower temperatures. The significant chemical bonding nature associated with the coloring/bleaching process which follows the H⁺ ion incorporation in the film is studied by FTIR analysis. The W–O–W framework peak was observed at 563 cm⁻¹ and confirms the stability of the films in the electrochemical analysis. The results obtained from cyclic voltammetry technique and ECD cell characterization are used to emphasize the suitability for some applications of the solar control systems.

1. Introduction

The electrochromic properties of tungsten oxide (WO₃) films have been widely investigated because of the potential applications in 'smart windows' or display devices and in electrochromic devices (ECDs) [1]. A thin film of WO₃,

containing W⁶⁺, in its oxidized form, is colorless, but when a negative potential is applied to the electrode the film is reduced to W⁵⁺; the film becomes a deep blue in color. It can be reoxidized to colorless (original color) form by the application of more positive potential. Thus the film electrode surface can be repeatedly switched between two states of different colors. This phenomenon is called electrochromism and the materials are referred to as electrochromic materials.

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Such electrochromic materials may also be used for optical switching circuits [2].

The electrochromic phenomenon in WO_3 occurs when a voltage is applied between electrolytes containing M^+ ions ($\text{M} = \text{H}, \text{Li}, \text{Na}$ and K) and a film electrode (WO_3); the M^+ ions are inserted into WO_3 films. Tungsten bronze (M_xWO_3) is formed according to the following reaction mechanism:



In the present case $\text{M}^+ = \text{H}^+$ ions, that are injected into the film surface from the H_2SO_4 electrolyte solutions. The insertion and extraction of ions are called intercalation and deintercalation.

Although electrochromic devices have been employed to provide the user control of light transmission, such devices require an externally applied voltage to control the electrochromic behaviour. A major application of electrochromic materials is in the fabrication of 'smart windows'. Smart windows are active glazing devices that can be used to control the amount of visible and solar radiation entering a building, in order to minimize the building's energy load normally associated with heating, cooling and lighting. Electrochromic films undergo a color change by either 'reflectance modulation' or 'absorption modulation' [1]. Reflectance modulation results from an increase in the free electron density in the material [3] and is observed in crystalline electrochromic materials. Amorphous electrochromic materials exhibit absorption modulation, caused by the development of an absorption band [4]. Crystalline electrochromic films have significantly lower ionic mobility than amorphous films, which limits the maximum switching speed, and these films are also difficult to produce in combination with other layers. As tungsten oxide crystallizes, it changes its electronic structure from tungsten ions with localized charge carriers to a Drude-type metallic tungsten bronze [5]. On the other hand, with crystallization the structure not only becomes ordered but increases in density, which is known to inhibit the electrochromism. Amorphous electrochromic layers are therefore preferable for smart window components. Moreover, there are several conflicting conclusions on this topic in the literature. The particular conclusions are the following:

- (i) crystalline films hardly color, hence have poor electrochromic properties [6];
- (ii) crystallinity does not affect the electrochromic properties of the films [7];
- (iii) substrate temperature must be kept as low as possible to obtain high coloration efficiency [8].

The fabrication of electrochromic devices is the most popular technology for large area switching devices. In the past, there used to be only two types of electrochromic devices. In the first type, the electrodes were made of conducting glass and covered with an organic or inorganic polymer. The two materials would usually display complementary electrochromism and hence produce the same color change when one is oxidized while the other is reduced. This type of construction was used in electrochromic windows. It is bistable, which means that once the color change has occurred,

the state of the device remains even in the absence of applied voltage. The limitation in this type of electrochromic devices is the slowness of the color change, due to the low migration rate of the counter-ions in the bulk polymer. It is also difficult to obtain strong color changes or bright colors.

In the second type, two complementary electrochromic molecules are dissolved in a solvent. This type of system is very simple to build, reacts very fast and can produce dark or bright colors. The drawback of this type is that an electrical current is needed to maintain the colored state because the two types of colored molecules diffuse through the system and react with each other to restore the bleached states. It cannot therefore be used for large area devices or for battery-powered displays.

In order to overcome these problems, we therefore need a system which is both bistable, and changes the color rapidly. The above processes can be achieved by attaching a suitable molecule that is colorless in the oxidized state and colored in the reduced state onto the surface of a colorless semiconducting electrochromic material (present case, WO_3) on conducting glass (present case, FTO substrates). When a sufficiently negative potential is applied, electrons are injected from the conducting glass into the conduction band of the semiconducting electrochromic material and reduce the absorbed molecules. The reverse process occurs when a positive potential is applied and the molecules are bleached. The advantage of this system is that it combines immobility of the electrochromic material with the rapidity and coloration efficiency of molecular systems.

Various techniques, such as spray pyrolysis [9], electrodeposition [10], thermal evaporation [11] and electron beam evaporation [12], have been adopted for the preparation of WO_3 films on different substrates. In this work, we have prepared the WO_3 films on microscopic glass and conducting glass (fluorine doped tin oxide ($\text{SnO}_2:\text{F}$ or FTO) coated glass) substrates by using the electron beam evaporation technique. However, the deposition methods and their conditions influence the considerable differences in structural, surface morphological, optical and electrochemical properties. By controlling these parameters, one could design a material with suitable electrochromic behaviour for device applications. In our earlier work we have reported the detailed description for the preparation of WO_3 films by the electron beam evaporation technique and their systematic characterization studies like structural, surface morphological and optical properties [13–15].

In the present work, we attempted to study the compositional and electrochemical analyses by x-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV), respectively. The electrochemical performance of WO_3 films was studied by intercalating/deintercalating H^+ ions from H_2SO_4 electrolyte solutions in the configuration of $\text{SnO}_2:\text{F}/\text{WO}_3/\text{H}_2\text{SO}_4/\text{Pt}$, SCE. The electrochemical nature of WO_3 films by inserting H^+ ions was studied by different authors [16, 17]. The electrochromic device performance of the films was also studied by constructing the three electrode electrochromic device (ECD) cells. The various electrochemical parameters like cathodic spike current (i_{pc}), anodic peak current (i_{pa}), diffusion coefficient (D), optical density (OD) and coloration efficiency (CE) of the films are evaluated and tabulated. The chemical bonding nature of interca-

lated/deintercalated (H⁺ ion) films was tested from the FTIR analysis.

2. Experimental details

2.1. Film preparation

The films of WO₃ were deposited by the electron beam evaporation technique using a HINDHIVAC vacuum coating unit (model 12A4D) with electron beam power supply (model EBG-PS-3K). Samples of dry WO₃ powder (99.99%) were made into pellets, placed in a graphite crucible and kept on the water-cooled copper hearth of the electron gun. These samples (pellets) were heated with a 180° deflected electron beam from the tungsten filament of the electron gun with the accelerating voltage of 5 kV and a power density of about 1.5 kW cm⁻². The WO₃ pellets were evaporated in a pressure of about 1 × 10⁻⁵ mbar and then deposited as thin films on the microscopic glass and conducting fluorine doped tin oxide coated glass substrates (FTO). Rotation of the substrate during the deposition process yielded uniform deposition of the films. The depositions were carried out at different substrate temperatures (T_{sub}), i.e., room temperature (30 °C, RT), 100 °C and 200 °C. The room-temperature-prepared films were further annealed at 200 and 300 °C for about 1 h in a vacuum environment.

2.2. Characterization

The thickness of these films was measured using a stylus instrument (Mitutoyo surface profilometer). The thickness of WO₃ films deposited at different substrate temperatures like 30 °C, 100 °C and 200 °C are 0.60, 1.28 and 1.70 μm, respectively. X-ray photoelectron spectroscopy (XPS) studies were carried out by a VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatized Mg Kα x-ray source with the energy of 1253.6 eV. Base pressure in the analysis chamber was 4 × 10⁻¹⁰ Torr. A multichannel detection system with nine channels was used to collect the data. The electrochemical analysis of the films was carried out by the cyclic voltammetry technique using the EG & G Princeton Applied Research potentiostat/galvanostat model 273A with EG & G interface model 507. The optical transmission measurements were carried out by a Hitachi-3400 UV-vis-NIR spectrometer in the wavelength range from 300 to 2500 nm. The IR investigations of the films were performed by using a Perkin-Elmer Paragon FTIR spectrometer (model 500) in the range 4000–400 cm⁻¹.

3. Results and discussion

3.1. X-ray photoelectron spectroscopic (XPS) study

Electron spectroscopy for chemical analysis (ESCA) (or) x-ray photoelectron spectroscopy (XPS) is a widely used analytical surface-sensitive technique for investigating the chemical composition of thin solid films. The qualitative XPS survey scan analyses the WO₃ films obtained in 0–1000 eV binding energy (E_b) range. The survey scan information is useful, particularly in the identification of the elements present at the film surface. The x-ray photoelectron spectroscopy survey scan of the electron beam evaporated WO₃ films prepared on

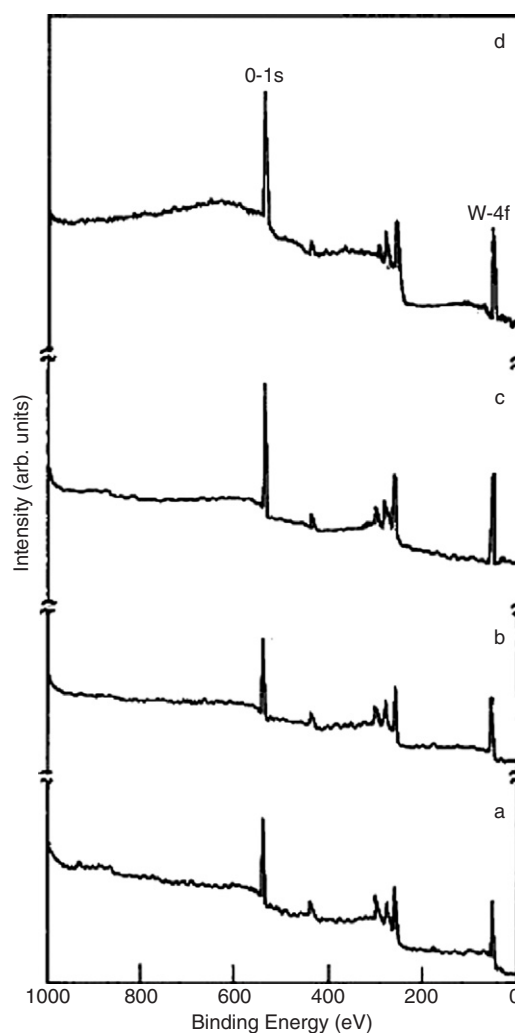


Figure 1. X-ray photoelectron spectroscopy survey scan of WO₃ films on glass substrates: (a) $T_{\text{sub}} = \text{RT}$, (b) $T_{\text{sub}} = 100\text{ }^\circ\text{C}$, (c) $T_{\text{sub}} = 200\text{ }^\circ\text{C}$ and (d) $T_{\text{anne}} = 300\text{ }^\circ\text{C}$.

glass substrates at $T_{\text{sub}} = \text{RT}$, $T_{\text{sub}} = 100\text{ }^\circ\text{C}$, $T_{\text{sub}} = 200\text{ }^\circ\text{C}$ and $T_{\text{anne}} = 300\text{ }^\circ\text{C}$ is shown in figures 1(a)–(d), respectively. From the XPS spectra (figure 1), the WO₃ films prepared in the present work seem to be not contaminated, since there is no peak other than the characteristic peaks of W and O. This enumerated the compositional purity and quality of deposited films.

The proposed electrochromic mechanism of WO₃ films is based on the existence of different final states, screened by different numbers of W 5d electrons. The W⁶⁺, W⁵⁺ and W⁴⁺ states have the 4f^{1/2} 5d⁰, 4f^{1/2} 5d¹ and 4f^{1/2} 5d² configurations, respectively. There are more outer electrons for the four-valent tungsten than for both the six-valent and five-valent tungsten. The outer electronic screening effect of the four-valent tungsten is bigger than that of the six-valent and five-valent tungsten. The binding energies (E_b) of tungstens with different valencies are arranged as follows:

$$E_b(\text{W}^{4+}) < E_b(\text{W}^{5+}) < E_b(\text{W}^{6+}). \quad (2)$$

Hollinger *et al* [18] reported that the XPS 4f^{7/2} peaks located at +4.5, +3 and +1.5 eV from the metallic tungsten 4f^{7/2}

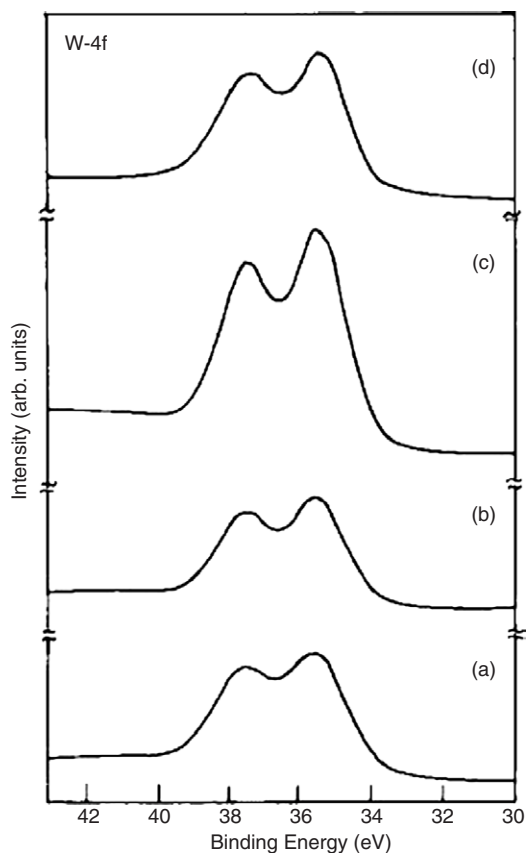


Figure 2. X-ray photoelectron spectroscopy spectra of the W 4f doublet core level of WO_3 films: (a) $T_{\text{sub}} = \text{RT}$, (b) $T_{\text{sub}} = 100^\circ\text{C}$, (c) $T_{\text{sub}} = 200^\circ\text{C}$ and (d) $T_{\text{anne}} = 300^\circ\text{C}$.

peak W^0 can be attributed to W^{6+} , W^{5+} and W^{4+} states, respectively. The $4f^{7/2}$ peak of metallic W is located at 31.5 eV [19].

Figures 2 and 3 show the corresponding occurrence of structured tungsten (W 4f) and oxygen (O 1s) peaks for the WO_3 films under the same conditions as for the XPS survey scan of figure 1. From the XPS core-level spectra of W 4f (figures 2(a)–(d)), the doublet was observed at E_b of 35.53 and 37.6 eV corresponding to W $4f_{7/2}$ and W $4f_{5/2}$, respectively. They are in good agreement with those of tungsten (VI) trioxide powder [20]. Therefore, it is evident that the tungsten (W) in the electron beam evaporated WO_3 film is present in the six-valent state (W^{6+}). Lianyong Su *et al* [21] also observed W $4f_{7/2}$ and W $4f_{5/2}$ core levels at 35.8 and 37.9 eV, respectively. They also reported the presence of six-valent tungsten (W^{6+}) in electrodeposited WO_3 films. The W 4f core-level spectrum of WO_3 films prepared at room temperature (figure 2(a)) is broader. From this broadening effect it may be concluded that as-deposited room temperature films are not fully oxidized, i.e. they contain small amounts of W^{5+} . This is in agreement with the fact that these films are slightly more absorptive than the higher temperature prepared films and also the annealed films, which indicates the amorphous nature of as-deposited room-temperature-prepared films. This was also confirmed from the x-ray diffraction analysis [13]. Nevertheless, the absorbance is quite small and cannot be correlated with the amount of W^{5+} ,

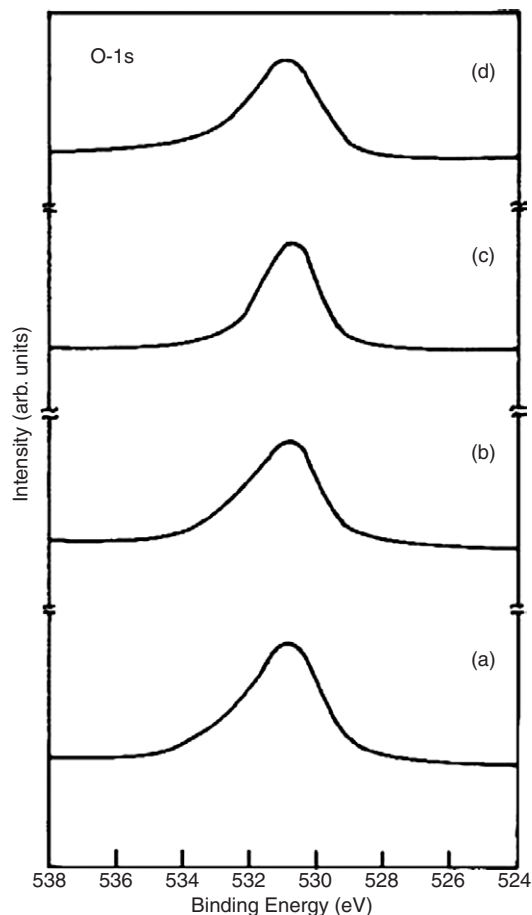


Figure 3. X-ray photoelectron spectroscopy spectra of the O 1s core level of WO_3 films: (a) $T_{\text{sub}} = \text{RT}$, (b) $T_{\text{sub}} = 100^\circ\text{C}$, (c) $T_{\text{sub}} = 200^\circ\text{C}$ and (d) $T_{\text{anne}} = 300^\circ\text{C}$.

which means that evaporated amorphous WO_3 films possess a substoichiometry which does not contribute to the optical absorbance. When the substrate temperature was increased to 200°C , the core-level peaks (figure 2(c)) become sharper and better resolved, indicating an improvement in the crystallinity of film. The same well resolved peak (figure 2(d)) was observed from the films prepared at $T_{\text{sub}} = \text{RT}$ and further annealed at 300°C .

The characteristic peak position for the O 1s core level of WO_3 films prepared in the present work (figure 3) is quite close to the binding energy (E_b) of 530.86 eV, which agrees well with the literature reported earlier [22]. A quantitative analysis of the oxygen and tungsten atomic concentration was carried out for the deposited films and they are summarized along with their core-level binding energies in table 1. The W and O atomic concentration of room temperature prepared films is found to be equal to 21.2% and 78.8%, respectively, whereas in the case of films prepared at higher substrate temperature, i.e. 200°C , the W and O concentration is 31.63% and 68.37%, respectively. It is evident that the stoichiometric formulation of the prepared WO_3 films is close to stoichiometry of WO_3 , within an estimated error. It is clearly observed from table 1 that the concentration of oxygen decreases with increasing substrate and annealing temperatures, which enumerates the formation of oxygen ion vacancies in the films. This also

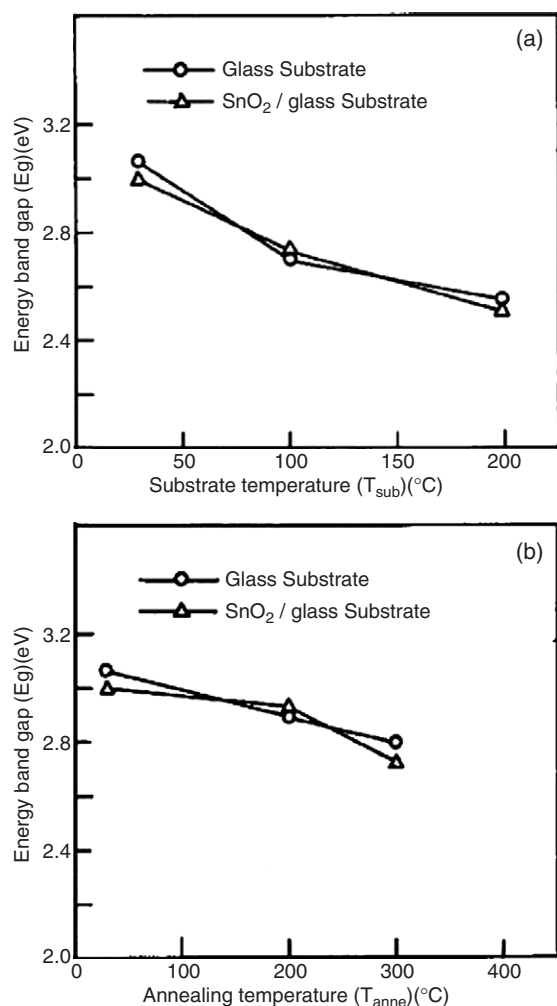


Figure 4. Variation of energy bandgap, E_g , of WO₃ films, (a) with respect to substrate temperatures and (b) with respect to annealing temperatures.

causes a slight decrease in optical transmission and energy bandgap of the films. Figures 4(a) and (b) show the decrease in optical energy bandgap with increasing substrate and annealing temperatures evaluated from the optical absorbance spectrum [13, 14]. Thus, the obtained results of compositional analysis are supported with our earlier work.

3.2. Studies for electrochromic response

(a) *Cyclic voltammetric analysis.* In this investigation, we also concentrate on studying the electrochemical nature of the films for the electrochromic device applications. The electrochemical behaviour of the films was tested by inserting H⁺ ions through a three-electrode electrochemical cell using an electrolyte containing 0.05 and 0.1 M H₂SO₄ electrolyte solutions. In the electrochemical cell the WO₃ films on FTO substrates were used as working electrodes and a saturated calomel electrode (SCE) and platinum wire were used as reference and counter-electrodes, respectively. Figure 5 shows a schematic diagram of the cyclic voltammetric set-up. The ion intercalation (i.e. coloration process) and deintercalation (i.e. bleaching process) were performed at different scan rates,

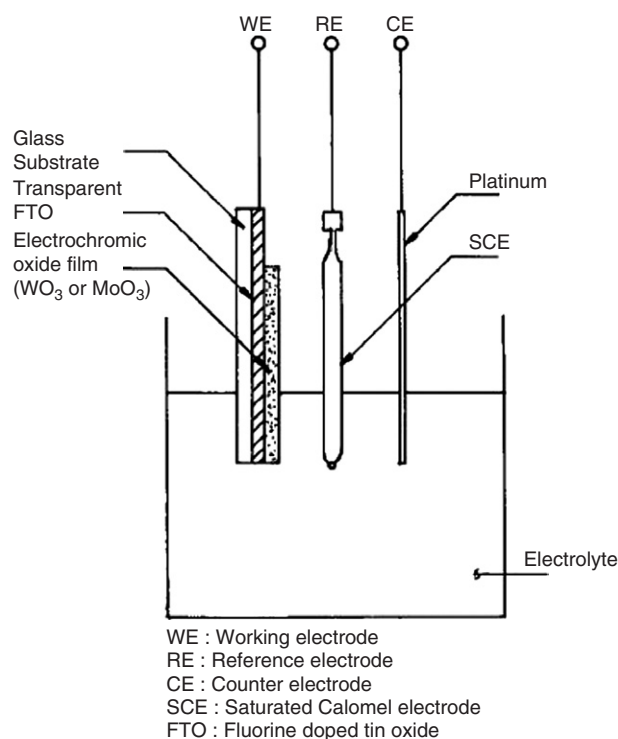


Figure 5. Schematic illustration of cyclic voltammetry set-up.

Table 1. XPS curve fitting analysis of W (4f) and O (1s) core levels at various temperatures with literature values.

Sample	Binding energy E_b (eV)			Atomic concentration (%)	
	W 4f _{7/2}	W 4f _{5/2}	O 1s	W	O
WO ₃ /glass/ T_{sub} RT	35.53	37.6	530.86	21.20	78.80
WO ₃ /glass/ T_{sub} 100 °C	35.53	37.6	530.86	22.27	77.73
WO ₃ /glass/ T_{sub} 200 °C	35.53	37.6	530.86	31.63	68.37
WO ₃ /glass/ T_{anne} 300 °C	35.53	37.6	530.86	26.15	73.85
Literatures	35.8 ^a 35.4 ^b —	37.9 ^a 37.6 ^b —	— — 530.6 ^c	— — —	— — —

^a Reference [21].

^b Reference [10].

^c Reference [22].

like 100, 200 and 300 mV s⁻¹. The current resulting from these scan rates is cathodic current (i_{pc}), which is associated with the coloring process of the film, and the anodic current (i_{pa}) is associated with the bleaching process. The cyclic voltammograms of the films were recorded in the potential (E) range from -1.0 to +1.0 V_{SCE}. During the negative potential of the scan we observed a dark blue coloration of the films at -1.0 V_{SCE}, whereas the films become colorless in the positive potential, i.e. bleaching occurred at +1.0 V_{SCE}. This coloration ↔ bleaching mechanism of WO₃ films confirms the perfect electrochromic nature of the films associated with the

Table 2. Electrochemical parameters of WO₃ films associated with intercalation–deintercalation of H⁺ ions cycled in 0.05 M H₂SO₄ electrolyte solution.

Sample	Scan rate, ν (mV s ⁻¹)	Cathodic spike current, i_{pc} (mA)	Anodic peak current, i_{pa} (mA)	Diffusion coefficient, D (cm ² s ⁻¹)	
				For i_{pc}	For i_{pa}
WO ₃ /RT	100	16.25	8.75	1.42×10^{-7}	4.13×10^{-8}
	200	20.00	17.50	1.08×10^{-7}	8.27×10^{-8}
	300	21.25	21.25	8.13×10^{-8}	8.13×10^{-8}
WO ₃ /100 °C	100	10.28	3.42	5.71×10^{-8}	6.32×10^{-9}
	200	11.57	6.85	3.61×10^{-8}	1.26×10^{-8}
	300	12.57	9.71	2.84×10^{-8}	1.69×10^{-8}
WO ₃ /200 °C	100	5.90	1.00	1.88×10^{-8}	5.40×10^{-10}
	200	7.00	4.09	1.32×10^{-8}	4.52×10^{-9}
	300	9.36	6.00	1.57×10^{-8}	6.48×10^{-9}
WO ₃ /RT/ T_{anne} : 200 °C	100	7.27	2.78	2.85×10^{-8}	4.17×10^{-9}
	200	9.69	6.90	2.53×10^{-8}	1.28×10^{-8}
	300	10.42	9.45	1.95×10^{-8}	1.60×10^{-8}
WO ₃ /RT/ T_{anne} : 300 °C	100	5.40	0.45	1.57×10^{-8}	1.09×10^{-10}
	200	5.68	1.27	8.72×10^{-9}	4.36×10^{-10}
	300	6.00	1.50	6.48×10^{-9}	4.05×10^{-10}

Table 3. Electrochemical parameters of WO₃ films associated with intercalation and deintercalation of H⁺ ions cycled in 0.1 M H₂SO₄ electrolyte solution.

Sample	Scan rate, ν (mV s ⁻¹)	Cathodic spike current, i_{pc} (mA)	Anodic peak current, i_{pa} (mA)	Diffusion coefficient, D (cm ² s ⁻¹)	
				For i_{pc}	For i_{pa}
WO ₃ /RT	100	11.4	4.0	1.75×10^{-8}	2.16×10^{-9}
	200	13.7	6.1	1.26×10^{-8}	2.51×10^{-9}
	300	15.1	6.5	1.02×10^{-8}	1.90×10^{-9}
WO ₃ /100 °C	100	9.0	2.0	1.09×10^{-8}	5.40×10^{-10}
	200	9.6	3.1	6.22×10^{-9}	6.49×10^{-10}
	300	10.6	4.0	5.06×10^{-9}	7.20×10^{-10}
WO ₃ /200 °C	100	7.1	1.5	6.81×10^{-9}	3.04×10^{-10}
	200	8.0	2.0	4.32×10^{-9}	2.70×10^{-10}
	300	8.7	2.9	3.41×10^{-9}	3.78×10^{-10}
WO ₃ /RT/ T_{anne} : 200 °C	100	8.2	2.4	9.08×10^{-9}	7.78×10^{-10}
	200	9.7	4.0	6.35×10^{-9}	1.08×10^{-9}
	300	11.1	5.3	5.55×10^{-9}	1.26×10^{-9}
WO ₃ /RT/ T_{anne} : 300 °C	100	6.3	1.7	5.36×10^{-9}	3.90×10^{-10}
	200	7.7	3.0	4.00×10^{-9}	6.08×10^{-10}
	300	9.4	4.4	3.98×10^{-9}	8.72×10^{-10}

electrochemical intercalation and deintercalation of H⁺ ions and electrons into WO₃ lattice. The films have the capability to withstand all the scan rates and also up to 1×10^3 cycles of coloration/bleaching. It is emphasized that WO₃ films prepared in the present work may be one of the best candidates for ECD.

Figures 6(a)–(e) show the cyclic voltammograms of WO₃ films deposited at different temperatures like $T_{sub} = RT$, $T_{sub} = 100^\circ C$, $T_{sub} = 200^\circ C$, $T_{anne} = 200^\circ C$ and $T_{anne} = 300^\circ C$, cycled in 0.05 M H₂SO₄ electrolyte solutions, respectively. The corresponding cyclic voltammograms of WO₃ films cycled in 0.1 M H₂SO₄ electrolyte solutions are shown in figures 7(a)–(e). Each sample can be cycled at different scan rates like 100, 200 and 300 mV s⁻¹. It is observed that the magnitudes of both i_{pc} and i_{pa} increase with the increasing scan rates. It is to be noted that the intercalation/deintercalation of H⁺ ions is enhanced with the increasing scan rates. Thus, the films can be reversibly made transparent by electrochemical oxidation and colored

by reduction in a proton containing solution according to equation (1). In the electrochemical experiments, the performance of the films was evaluated from the diffusion coefficient (D) value of the inserted ions. In this case we have calculated the diffusion coefficient of the H⁺ ion by using Randle's Servcik equation [16].

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

where D is the diffusion coefficient, C_0 is the concentration of active ions in the electrolyte solution, ν is the scan rate, i_p is the peak current (both i_{pc} and i_{pa}) and n is the number of electrons and it is assumed to be unity. Tables 2 and 3 show the extracted electrochemical parameters of WO₃ films cycled in 0.05 and 0.1 M H₂SO₄ electrolyte solutions, respectively. They show that the diffusion coefficient values of WO₃ films in the H⁺ ion intercalation/deintercalation from 0.05 M H₂SO₄ electrolyte solutions vary between 5.40×10^{-10} and 1.42×10^{-7} cm² s⁻¹, whereas the D values vary from $8.72 \times$

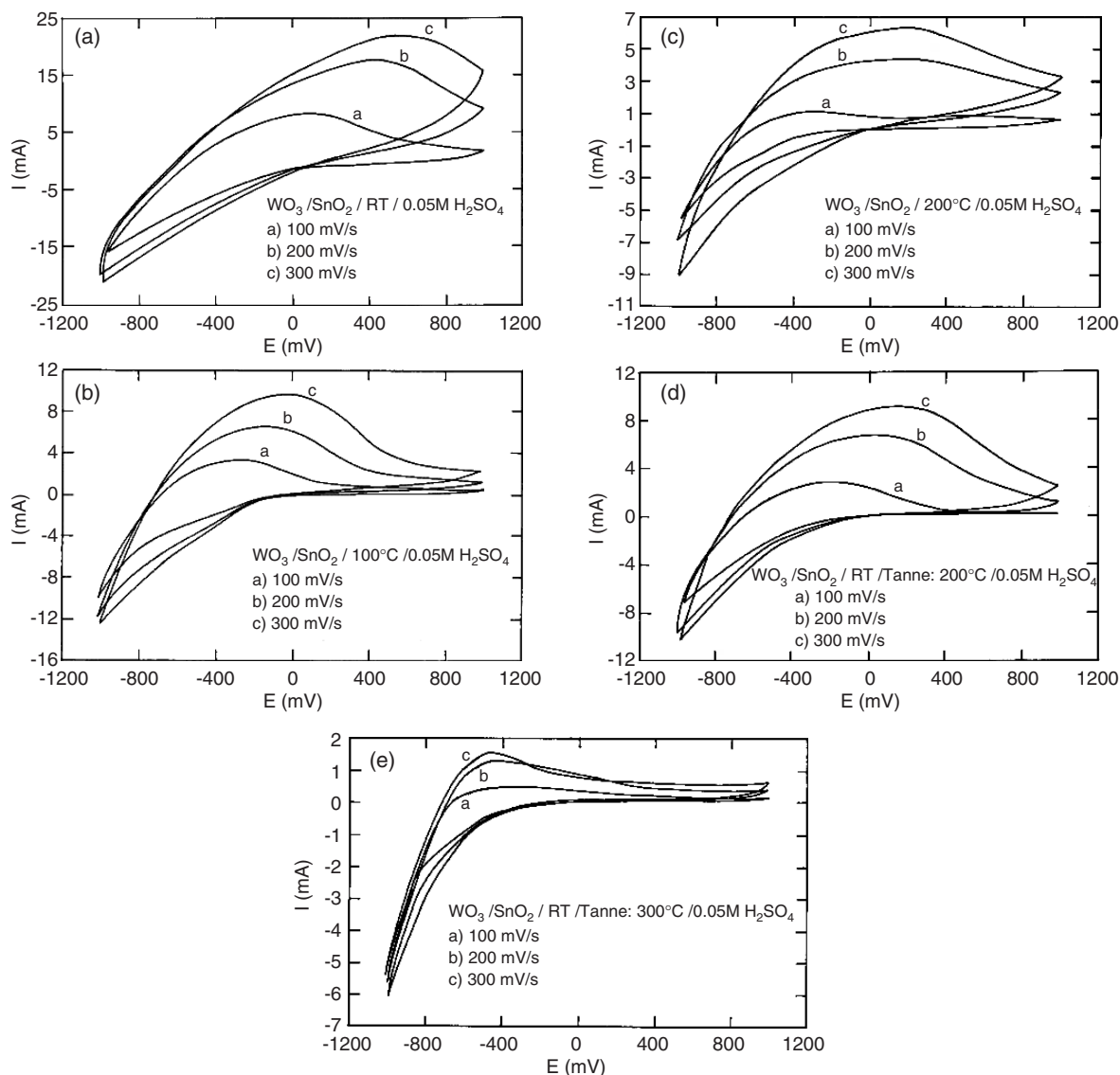


Figure 6. Cyclic voltammograms of WO₃ films prepared at different conditions, cycled in 0.05 M H₂SO₄ electrolyte solutions: (a) $T_{\text{sub}} = \text{RT}$, (b) $T_{\text{sub}} = 100^\circ\text{C}$, (c) $T_{\text{sub}} = 200^\circ\text{C}$, (d) $T_{\text{anne}} = 200^\circ\text{C}$ and (e) $T_{\text{anne}} = 300^\circ\text{C}$.

10^{-10} to $1.75 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for 0.1 M electrolyte solutions. Diffusion coefficient values for H⁺ ion intercalation/deintercalation of the order of 10^{-10} – $2.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ were reported by Bohnke *et al* [23] for the evaporated WO₃ thin films. Patil *et al* [16] reported the diffusion coefficient is of the order of $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for H₂SO₄ electrolyte solution and suggested that the D values of WO₃ films range from 1×10^{-9} to $21 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, depending on the preparation technique of the films. From this, we conclude that the obtained diffusion coefficient values in the present work are in accordance with the reported values. Even though the extent of H⁺ ion intercalation/deintercalation of WO₃ films is still active in higher temperature produced films, the magnitudes of both i_{pa} and i_{pc} and also the electrochemical performance are slightly less in the films produced at higher substrate and annealing temperature than the RT-deposited films.

(b) *Electrochromic device (ECD) cell characterization.* Followed by the cyclic voltammetry analysis, the device performance of WO₃ films have been tested by constructing the electrochromic device (ECD) cell. The basic and schematic design of the ECD cell is shown in figure 8. Typical electrochromic devices consist of the following: the working electrode (WE) was the FTO bearing the electrochromic film, while the counter-electrode (CE) was the other FTO plate. Platinum wire acted as a pseudo-reference electrode (RE) and was placed equidistant between the CE and WE. For coloring, an external voltage is applied. Electrons are injected into the electrochromic layer from the FTO and cations, i.e. M⁺, from the electrolyte. The reverse happens for the bleaching process. The electron-transfer reaction occurs within thin films of electrochromic oxide (WO₃) sandwiched between a transparent electrode of fluorine doped tin oxide (FTO) coated glass substrates and an electrolyte, which allows for ready conduction of the M⁺ ions (H⁺ or K⁺ or Li⁺) needed for

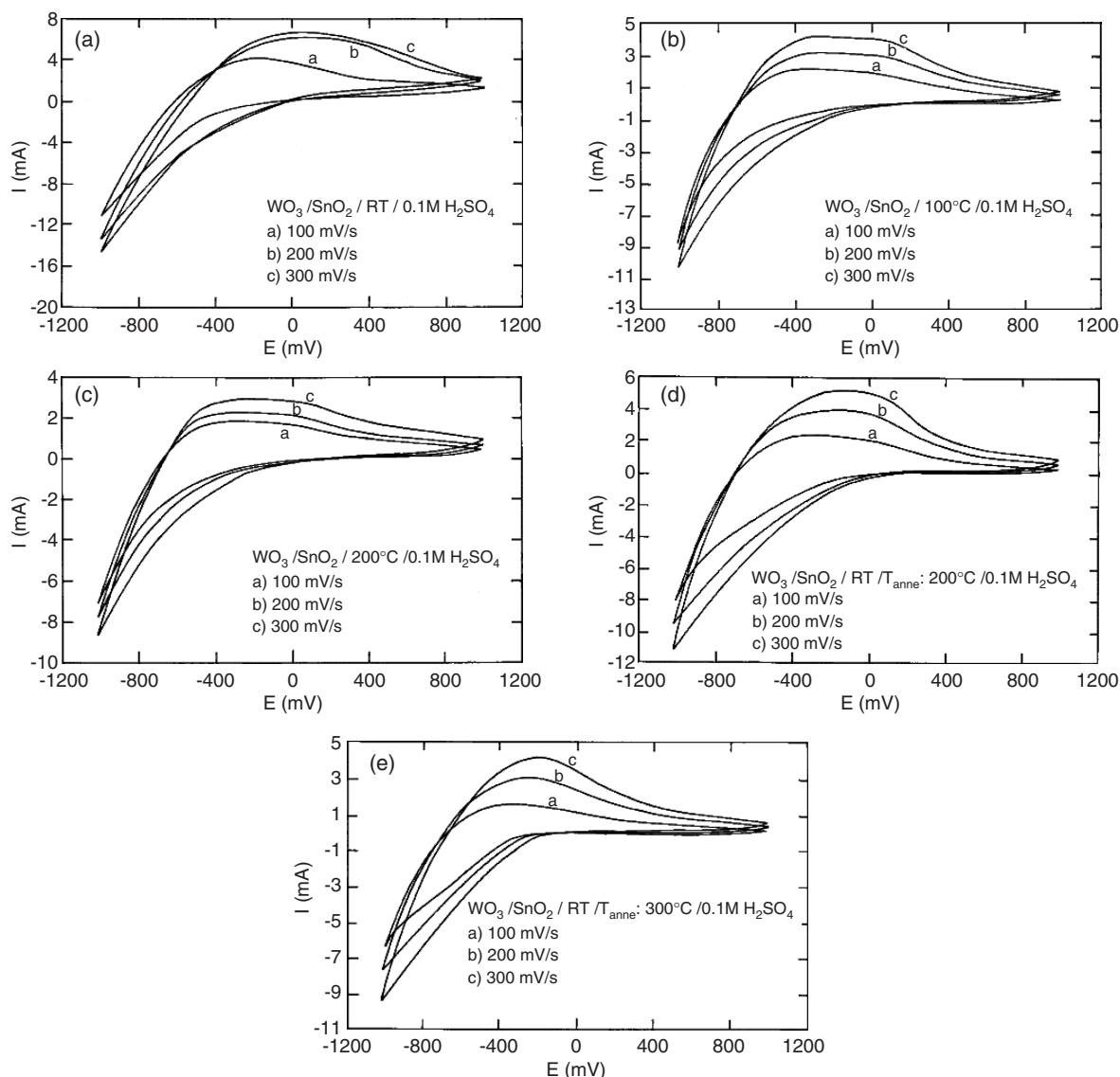


Figure 7. Cyclic voltammograms of WO_3 films cycled in 0.1 M H_2SO_4 electrolyte solutions: (a) $T_{\text{sub}} = \text{RT}$, (b) $T_{\text{sub}} = 100^\circ\text{C}$, (c) $T_{\text{sub}} = 200^\circ\text{C}$, (d) $T_{\text{anne}} = 200^\circ\text{C}$ and (e) $T_{\text{anne}} = 300^\circ\text{C}$.

charge balance in solid-solution electrodes; this arrangement with protons for M^+ , can be expressed as



Simple and clear illustrations of the electrochromic devices are shown schematically in the literature [24–26].

The change in optical transmittance of the colored and bleached films was studied by using a UV–vis–NIR spectrophotometer. In order to observe the changes in optical transmittance spectra of colored and bleached films as a function of substrate and annealing temperatures, the optical density (OD_λ) was evaluated. The coloration efficiency (CE) is also one of the very important parameters in electrochromic devices to identify the electrochemical performance of the films.

The optical density (OD) of the films was calculated from transmittance spectrophotometry [27] by

$$\text{OD}_\lambda = \log \left(\frac{T_{0\lambda}}{T_{x\lambda}} \right) \quad (4)$$

where $T_{0\lambda}$ is the reference transmittance and $T_{x\lambda}$ is the measured transmittance. We choose the reference transmittance as the bleached state, then the expression for optical density is [4]

$$\text{OD}_\lambda = \log \left(\frac{T_{b\lambda}}{T_{c\lambda}} \right) \quad (5)$$

where $T_{b\lambda}$ is the bleached transmittance at wavelength λ and $T_{c\lambda}$ is the colored transmittance at wavelength λ .

The coloration efficiency (CE) is defined by

$$\text{CE} = \frac{\text{OD}}{Q_{\text{in}}} \quad (6)$$

where OD is the optical density given by equation (5) and Q_{in} (mC cm^{-2}) is the charge injected during the coloration cycle.

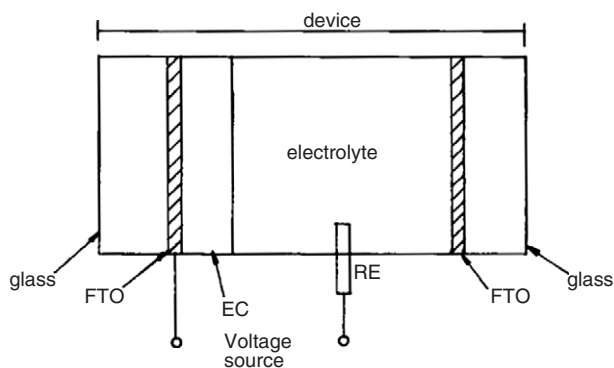


Figure 8. Schematic inset of electrochromic device (ECD) cells.

The optimized WO₃ films deposited on fluorine doped tin oxide coated (FTO or SnO₂:F) glass substrates by the electron beam evaporation technique have been employed as working electrodes in the electrochromic devices. The electrochromic performance of WO₃ films prepared at conditions $T_{\text{sub}} = \text{RT}$, $T_{\text{sub}} = 200^\circ\text{C}$ and $T_{\text{anne}} = 300^\circ\text{C}$ was studied in the ECD cells. The optical transparency of these films was studied for their coloration and bleaching processes cycled in 0.1 M H₂SO₄ electrolyte solutions.

The optical transmittance spectra (in the wavelength range between 300 and 2500 nm) of WO₃ films prepared at $T_{\text{sub}} = \text{RT}$, 200°C and $T_{\text{anne}} = 300^\circ\text{C}$, cycled in 0.1 M H₂SO₄ electrolyte solution, are shown in figures 9(a), (b) and (c), respectively. From these transmission spectra of colored and bleached states, it is observed that all the films show good electrochromic coloration. The transmittance in the visible range has been found to be significantly different for the films in bleached and colored states though the shape has no apparent change. This effect could make them useful in electrochromic display device and smart window applications. The higher optical modulation was observed in the visible range of the spectra, whereas the lower optical modulation was observed in the infrared range. This effect may be due to the maximum optical absorption of WO₃ films in their coloration and bleaching process in the visible range, which enumerated the suitability of these films in electrochromic device and smart window applications. However, the films produced at 200°C exhibit a lower transmission range in the visible region compared to the film deposited at $T_{\text{sub}} = \text{RT}$ (30°C). The annealed films ($T_{\text{anne}} = 300^\circ\text{C}$) also show the lower range in their visible region. Light scattering due to large crystal grains is thought to be the reason for the low transmittance, and its electrochromic properties may be influenced by the reaction between FTO and WO₃ films. Washizu *et al* [28] studied the relationship between optical and electrochromic properties of WO₃ films prepared by RF reactive sputtering. They observed lower transmittance for the WO₃ films in their coloration and bleaching process for the films deposited at higher temperature (300°C and 500°C) than the room temperature prepared films and suggested that the reason is light scattering due to large crystal grains.

The optical density and coloration efficiency of the films were calculated at the wavelength range of about 633 and 1033 nm and they are clearly summarized in table 4. The

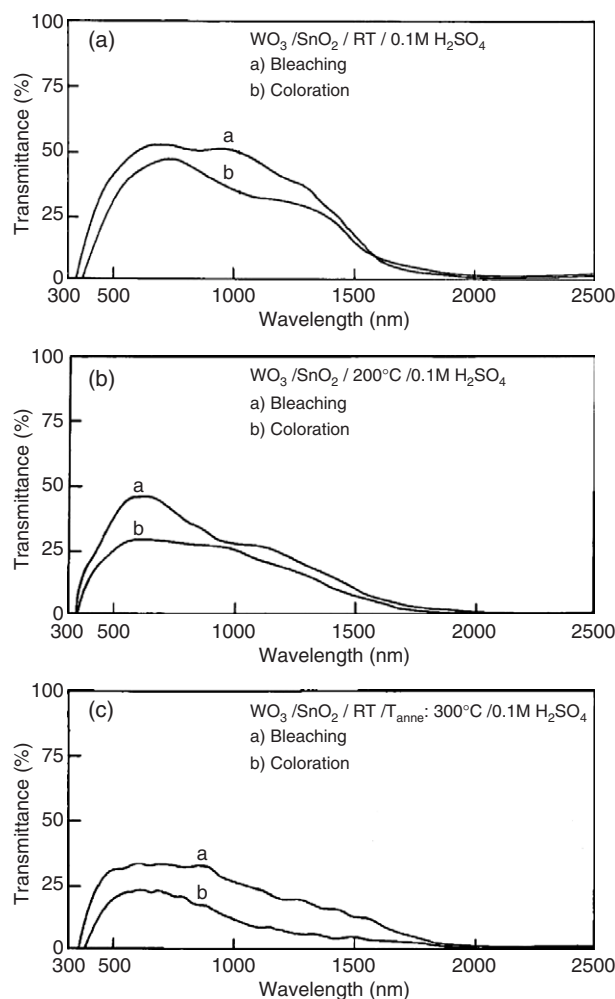


Figure 9. Optical transmittance spectra of WO₃ films in ECD cells, cycled by 0.1 M H₂SO₄ electrolyte solutions: (a) $T_{\text{sub}} = \text{RT}$, (b) $T_{\text{sub}} = 200^\circ\text{C}$ and (c) $T_{\text{anne}} = 300^\circ\text{C}$.

Table 4. Evaluated ECD cell parameters of WO₃ films in 0.1 M H₂SO₄ electrolyte solution.

Sample	Optical density OD		Coloration efficiency (CE) (cm ² C ⁻¹)	
	at $\lambda \sim 633$ nm	at $\lambda \sim 1033$ nm	at $\lambda \sim 633$ nm	at $\lambda \sim 1033$ nm
	WO ₃ /RT	0.10	0.17	18
WO ₃ /200°C	0.12	0.18	16	24
WO ₃ /RT/ T_{anne} : 300°C	0.17	0.44	8	20

corresponding graphical illustration of the evaluated OD and CE of WO₃ films is shown in figure 10. The evaluated optical density of WO₃ films lies in the range between 0.10 and 0.44, while the coloration efficiency is 8–32 cm² C⁻¹. The films produced at lower substrate temperature (i.e. $T_{\text{sub}} = \text{RT}$) have higher coloration efficiency than those obtained for the films produced at higher substrate temperature ($T_{\text{sub}} = 200^\circ\text{C}$) and annealing temperature ($T_{\text{anne}} = 300^\circ\text{C}$). Patil *et al* [16] reported that the coloration efficiency of spray deposited WO₃

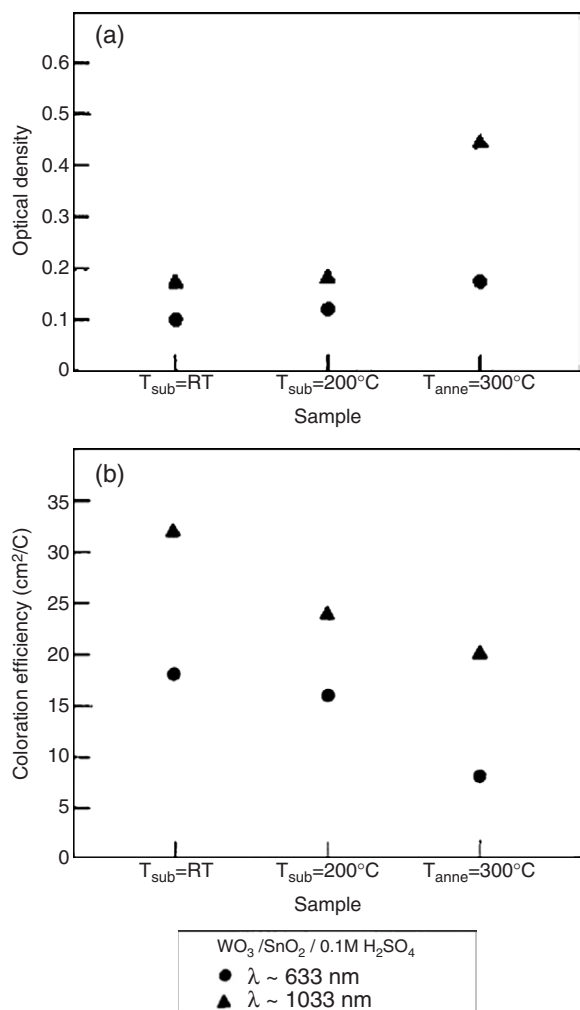


Figure 10. Variation of the electrochromic device parameters of WO₃ films with respect to substrate and annealing temperatures in 0.1 M H₂SO₄ electrolyte solutions: (a) optical density (OD) and (b) coloration efficiency (CE).

films varies between 40 and 56 cm² C⁻¹ at 633 nm. Kitao *et al* [8] observed a maximum coloration efficiency of 60 cm² C⁻¹ at 600 nm for a sample prepared at substrate temperature of 60 °C, compared to the result of Kaneko *et al* [29], who obtained a value of 24 cm² C⁻¹ for sputter deposition with a substrate temperature of 200 °C.

Our previous reports of WO₃ thin films [13–15] concluded that the films prepared at room temperature were amorphous in nature. When we increase the substrate temperatures (like 100 and 200 °C) (or) the room temperature films subjected to post-heat-treatment (annealing) at 200 and 300 °C for about 1 h in vacuum environment, we observed the improvement in crystallinity of the films. Optical properties of the films showed the decrease in transmittance value of the films with increasing substrate temperature and annealing temperature. It is also observed that there is a slight decrease in bandgap values of the films with increasing temperatures, which reconciled the formation of oxygen ion vacancies in the films with increasing substrate or annealing temperatures. The particle-induced x-ray emission spectroscopic studies also showed supportive results for these conclusions.

Our present x-ray photoelectron spectroscopic studies also show the decrease in concentration of the oxygen in the films with increasing temperature, which suggests the formation of oxygen ion vacancies in the films. From the result of electrochemical analysis it is observed that the films prepared at room temperature possess higher performance than the higher temperature prepared films and also annealed films. The decrease in electrochromic behaviour associated with crystallization is a well known effect, which is associated with the formation of a Drude-type metallic tungsten bronze on crystallization [5]. The small polaron absorption may be responsible for the coloration of amorphous tungsten oxide films. On the other hand, with crystallization the structure not only becomes ordered but increases in density, which is known to inhibit electrochromism. Miyake *et al* [6] conclude that the crystalline films have poor electrochromic properties. Lee *et al* [30] also studied the electrochromic behaviour of WO₃ films prepared by the sol-gel process and they suggested that the higher temperature of firing of the films leads to weak blue coloration, whereas the strong blue coloration is for the lower firing temperature. Hence it could be concluded that the electrochromic response of WO₃ films is strongly affected by the crystallinity of the films, influenced by substrate temperatures and other conditions during film preparation. Thus, it is found that the observed electrochemical performance like OD and CE in ECD cells is comparable with the results reported earlier, which enumerated the suitability of WO₃ films in electrochromic smart window applications.

3.3. FTIR analysis

In order to identify the bonding assignments of intercalated/deintercalated WO₃ films cycled in 0.1 M H₂SO₄ electrolyte solutions, the IR absorption spectroscopic analysis has been carried out using the Perkin-Elmer Paragon 500 FTIR spectrometer. Figures 11(a)–(c) show the IR absorption spectra of WO₃ films (intercalated/deintercalated in 0.1 M H₂SO₄ electrolyte) prepared at conditions T_{sub} = 30 °C, T_{sub} = 200 °C and T_{anne} = 300 °C, respectively. The peak observed at 563 cm⁻¹ confirms the vibrational properties of disordered tungsten-oxygen (W–O–W) framework [31]. This demonstrates the electron beam evaporated WO₃ films are highly stable in H₂SO₄ electrolytes after the coloration/decoupling process. The peak at 800–1000 cm⁻¹ is associated with W–O stretching and bending modes [17]. The absorption peaks at 1630 and 3420 cm⁻¹ may be attributed to interlayer H₂O and OH⁻ stretching modes, respectively [32]. The formation of these H₂O and OH⁻ peaks may be due to the aqueous electrolyte solutions. The hydroxyl ion peak was observed at about 2328 cm⁻¹. With increasing of substrate temperatures, the peak at 2328 cm⁻¹ was gradually weaker but did not vanish. The presence of W–O bonds was observed at 1427 cm⁻¹ [11] and the intensity of the peak gradually increases with increasing substrate temperature, attributed to the improvement in crystallinity and the changes in crystalline microstructure with the substrate temperature. The 3700 cm⁻¹ absorption peak is due to the coloration.

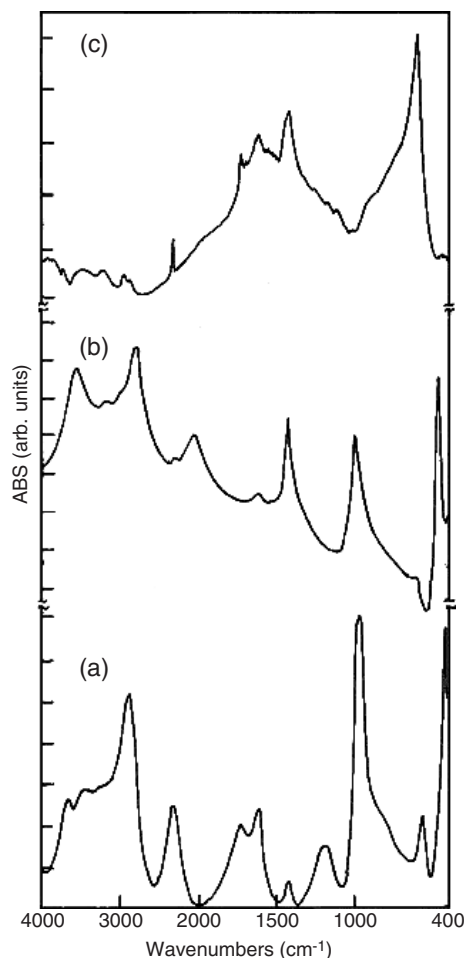


Figure 11. FTIR spectra of intercalated WO₃ films in 0.1 M H₂SO₄ electrolyte solutions: (a) $T_{\text{sub}} = \text{RT}$, (b) $T_{\text{sub}} = 200\text{ }^{\circ}\text{C}$ and (c) $T_{\text{anne}} = 300\text{ }^{\circ}\text{C}$.

4. Conclusions

This paper describes the electrochromic device applications of WO₃ films prepared by the electron beam evaporation technique. The effect of substrate temperature and heat treatment on the compositional and electrochromic properties was studied by x-ray photoelectron spectroscopy, cyclic voltammetry, optical and electrochemical techniques. The presence of six-valent tungsten (W⁶⁺) in the films has been confirmed from W 4f core level binding energies. The lack of oxygen in the film with increasing substrate and annealing temperatures enhanced the crystallization of the film from its amorphous state.

It is observed from the electrochemical analysis and ECD cell characterization that the performance of the films is high in the room temperature prepared films. The reason is that the lower substrate temperature minimizes the extent of crystallinity and favours the amorphous nature of the films. Hence, the amorphous films enhance the coloration efficiency. When the films turned to crystalline, the extent of coloration would be slight because

- (i) it is difficult for the counter-ions to enter the crystallites;
- (ii) difference in morphology: it is harder and therefore slower for a counter-ion to move through a more dense film.

Hence this reveals that the coloration efficiency and electrochemical performance of the films strongly depend on the preparative conditions, substrate temperature and annealing temperatures.

Thus in conclusion from our studies and results, we hope that the extracted data would be a massive scale in the applications of electrochromic windows.

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