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Current Applied Physics 3 (2003) 171–175

Current Applied Physics
Physics, Chemistry and Materials Science

www.elsevier.com/locate/cap

Structural, electrochromic and FT-IR studies on electrodeposited tungsten trioxide films

R. Vijayalakshmi [a], M. Jayachandran [b], C. Sanjeeviraja [c,*]

[a] *Department of Physics, Thiagarajar College, Madurai 625 009, India*
[b] *ECMS Division, Central Electrochemical Research Institute, Karaikudi 630 006, India*
[c] *Department of Physics, Alagappa University, Karaikudi 630 003, India*

Abstract

Tungsten trioxide (WO_3) has been found to be a very versatile material for electrochromic (EC) devices. It behaves as a mixed ion conductor and hence it has recently attracted much interest in the field of solid state ionics. When the intercalation of the film is taken in the cyclic voltammograms for various concentrations (0.1, 0.5 and 1.0 N) of H_2SO_4, the voltage is recorded for the peak current. The powder X-ray diffraction pattern is taken and the peaks are compared with the JCPDS values. It is found to be the triclinic structure. The FT-IR spectra are taken for the WO_3 films electrodeposited at different deposition current densities (0.25, 0.50, 0.65 and 0.75 mA/cm^2) keeping the other deposition parameters like pH of the solution, concentration of the electrolyte and temperature of the bath constant. The film exhibits a broad peak from 3780 to 3500 cm^{-1} which indicated the OH–H stretching vibration. The peak at 3543 cm^{-1} depends upon the coloration increase in the electrodeposited tungsten trioxide film. A little amount of molecular water may exist in the electrodeposited WO_3 film, which corresponds to a broad peak at 2500 cm^{-1}. A small peak at 820 cm^{-1} exhibits W–O stretching. After ion intercalation the peak positions are slightly changed.

PACS: 68.55; 81.55.L; 32.20
Keywords: Electrochromic; WO_3; Electrodeposition; FT-IR

1. Introduction

Tungsten trioxide (WO_3) has been found to be a very versatile material for electrochromic (EC) devices. The EC phase found to be hydrated $WO_3 \cdot xH_2O$ where x depends on the temperature of deposition. The coloration mechanism consists of a reversible electron transfer between W^{+6} and W^{+5} with the formation such as H^+ and K^+ according to the following reaction

$$WO_3 + xH^+ + xe^- \leftrightarrow H_xWO_3$$

During the color bleach (CB) process the redox reaction of the host material causes injection or ejection of both cation or anion and an electron. So it behaves as a mixed ion conductor and hence it has recently attracted much interest in the field of solid state ionics. When a group I ion M^+ ($M = H$, Li, Na or K) is electrolytically intercalated into a transparent WO_3 film a tungsten bronze M_xWO_3 with dark blue color is formed. This process is reversible and known as electrochemichromism [1]. There are several methods of making WO_3 film like spray pyrolysis [2], sputtering [3], thermal oxidation [4], RF sputtering [5] and electrodeposition [6]. Electrodeposition method is a low cost and cheapest method. In the electrodeposited films an ageing process, CB process cycling is found to be necessary to obtain stable and easy characteristics. Infrared absorption spectra of the film are changed during the ageing process as well as by the coloration, bleaching after completion of ageing. These changes in the IR bands will be described and discussed in this paper.

2. Experimental

The WO_3 films were prepared by electrodeposition technique having the bath of 0.2 M of tungsten powder mixed with hydrogen peroxide. The parameters like the concentration of the solution, pH, and current ranges were optimized. The electrodeposition method consists

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[*] Corresponding author.
E-mail address: sanjeeviraja@rediffmail.com (C. Sanjeeviraja).

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doi:10.1016/S1567-1739(02)00196-7

Table 1
Optimised parameter for the WO_3 electrodeposition

Sl. no.	Parameter	Value
1	Galvanostatic	0.5 mA
2	pH	2
3	Bath temperature	300 K
4	Concentration	0.1 N
5	Deposition time	90 min
6	Substrate	SnO_2 coated glass plate

of three electrode system, one is acting as the SnO_2 coated plate as working electrode (WE), other the platinum electrode as counter electrode (CE), and the third one is the saturated calomel electrode (SCE) as reference electrode (RE). Two grams of tungsten powder of 99% purity and 30% of hydrogen peroxide was mixed and a few drops of H_2SO_4 were added to avoid the effervescence produced in the solution. Then the stock solution was diluted to get the concentration of 0.1 N. The pH of the solution was maintained as 2.0 and the deposition current was fixed as 0.5 mA and the temperature was maintained at the room temperature. The stock solution was diluted to get the films as uniform and transparent. Table 1 shows the optimized deposition parameters for the well adherent, uniform and thick films, electrolyte of 1.0, 0.5, 0.1 N. Powder X-ray diffraction pattern for the samples were obtained using JEOL JDX803a X-ray diffractometer with Ni filtered CuKα radiation in the range 2θ from 20° to 80°. Ion intercalation and de-intercalation was performed by scanning potentiostat EG&G M6310 version 219. Electrochemical coloration was made in an electrolyte of 0.1, 0.5, 1.0 N H_2SO_4 solution with platinum as the CE. Coloration and bleaching cycles were performed by applying a DC potential of $\pm 1\ V_{SCE}$ between the CE and the WE. FT-IR spectra were measured in transmittance mode using JASCO CANVAS 460 PLUS spectrophotometer between 4000 and 400 cm^{-1}. The wavelength specifications for the instrument is 7800–360 cm^{-10} and the resolution of the spectrophotometer is varying from 0.9, 2.0, 4.0, 8.0, 16.0 cm^{-1}, the instrument has single beam optical system, the sample chamber has the dimensions 175 mm (W) $\times$ 255 mm (D) $\times$ 170 mm (H), center focus, the beam splitter has wide band width type, KBr, ceramic light source is used and the detector is DLATGS with AUTO gain switching. There is a window at the light exit port on the interferometer side of the sample chamber. The window transmits infrared rays and is coated with a special moisture proof material. If condensation forms on this window, the transparency of the window may be adversely affected. But for the thin film material the wrapper paper is cut, has the dimension of the sample chamber and the thin film is placed at the centre. For the reference (instead of using the KBr pellet), the transparent SnO_2 coated plate is placed at the centre. The laser used in this instrument is classified as a Class 2 laser according to laser equipment classification IEC825 (JISC6801). The laser beam is used to control the moving mirror and to check the alignment of the optical system.

3. Results and discussions

Films are prepared under the optimized conditions by galvanostatic route. Fig. 1 shows the X-ray diffractogram of the WO_3 film. The d values are compared with the reported JCPDS values. The agreement is good. All the peaks are identified. Benjamin Reichman and Bard [4] reported that the pair of peaks at $d = 2.64$ and 2.66 Å which is the characteristic property of the triclinic structure of the film, prepared by thermal oxidation method. Wang et al. [7] reported that $(h\,k\,l)$ indices (0 2 2) and (2 2 0) represent the triclinic structure of WO_3 by the DC magnetron sputtering which has the same indices for the electrodeposited WO_3 film. Schuster and Nguygen [8] reported $2\theta \sim 24°$ exhibits the crystalline nature of the WO_3 films which is obeying the peaks observed also in the electrodeposited film. All the $(h\,k\,l)$ indices of the chemical vapor deposited WO_3 film prepared by Maruyama and Arai [9] also had the same Miller indices of the electrodeposited film. Table 2 gives the comparison of d-values with the reported JCPDS [10] values.

Reversible CB cycles can be attained using the tungsten trioxide films as the WE. According to the double injection model, some amount of protons (and electrons) can be extracted during the first bleaching procedure. By repeating the (CB) cycles, the amount of injected protons introduced during coloration period becomes equal to that of extracted protons during subsequent bleaching periods [5]. Cyclic voltammetry studies have been performed in a three electrode elect-

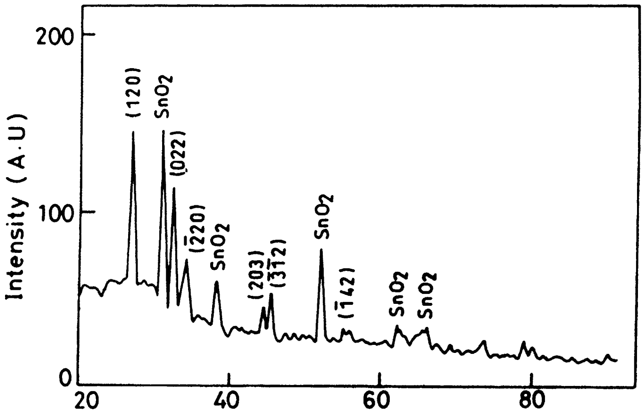

Fig. 1. XRD of the as-electrodeposited WO_3 film.

Table 2
Comparison of *d* values of as-electrodeposited WO_3 with JCPDS [10]

d (Å)		(*hkl*)
Experimental	JCPDS	
3.300	3.320	(1 2 0)
2.744	2.714	(0 2 2)
2.612	2.640	$(\bar{2}\,2\,0)$
2.039	2.080	(2 0 3)
1.992	1.986	$(\bar{3}\,\bar{1}\,2)$
1.668	1.665	$(\bar{1}\,4\,2)$

rochemical cell with WO_3/TCO glass as a WE and platinum electrode as the CE. The cyclic voltammograms in the range of −1.0 V_{SCE} to +1.0 V_{SCE} were obtained by various potential sweeps for 20 and 50 mV/s. The coloring and bleaching kinetics of the films was studied and the results revealed that neither coloring nor bleaching speeds are effected by the number of cycles. On the contrary the extent of coloring/bleaching and in particular the speed of bleaching depends, to a great extent, on film thickness. While thicker films exhibit the expected higher coloration, the coloring speed is not affected. The speed to a larger extent depends on film thickness and higher for thinner films [11]. Cyclic voltammograms of WO_3 films were measured in propylene carbonate (PC) electrolyte and the cathodic current is associated with bleaching [12]. The cathodic current is associated with the coloring process of the film and anodic current is following the scan reversal with bleaching. The starting potential where the cathodic current of the film begins to flow, was about +360 mV vs SCE for the as-deposited film, but the film stored in $LiClO_4$—PC electrolyte for 20 h at 70 °C was +50 mV vs SCE. The shift continued gradually with stage storage time after the initial drastic shift. These cathodic shifts result in the decrease of the injection charge in the coloring on reaction, which contributed to the degradation of EC activity of the WO_3 film. With respect to the anodic oxidation of the colored WO_3 film, the anodic reaction becomes fast with the storage of the film [13]. The WO_3 film obtained by vacuum evaporation method, a typical current–potential (*I*–*V*) curve of the WO_3 film electrode in 1 M H_2SO_4 was reported [4]. The cathodic coloration process is optically reversible and the reversal of the coloration process is relatively slow at the scan rate of 50 mV/s which is used. Our electrodeposited WO_3 film has best hydrogen ion injection in the normality of the electrolyte solution having 0.1, 0.5, 1.0 N. The potential scan starts from −1.2 V_{SCE} to +1.2 V_{SCE} and the scan rate is varying from 10 to 500 mV/s in steps of 10 mV/s. The WO_3 film has the efficiency to withstand for the entire scan rate, at the same time, during coloration, the film has very dark blue color. In bleaching section the color of the film is completely changed to colorless. The diffusion coefficient of H^+ ion during intercalation and de-intercalation is calculated from the Randles–Servcik equation

$$i_p = 2.72 \times 10^5 n^{3/2} D^{1/2} C_0 v^{1/2}$$

where D is the diffusion coefficient, C_0 is the concentration of active ions in the solution, v is the scan rate, n is the number of electrons and is assumed to be 1, i_p is the peak current density (anodic peak current i_{pa}, and cathodic peak current i_{pc}). Fig. 2 shows the ion intercalation–de-intercalation of WO_3 films. The values of i_p have been taken from Fig. 2. By substituting all the values, diffusion coefficient is calculated at 500 mV/s scan rate and is shown in Table 3. The diffusion coefficient and current density graphs for the electrodeposited film are comparable with the reported values.

IR absorption spectroscopy is a powerful technique particularly for elucidating changes in hydration and hydroxylation that occur upon ion

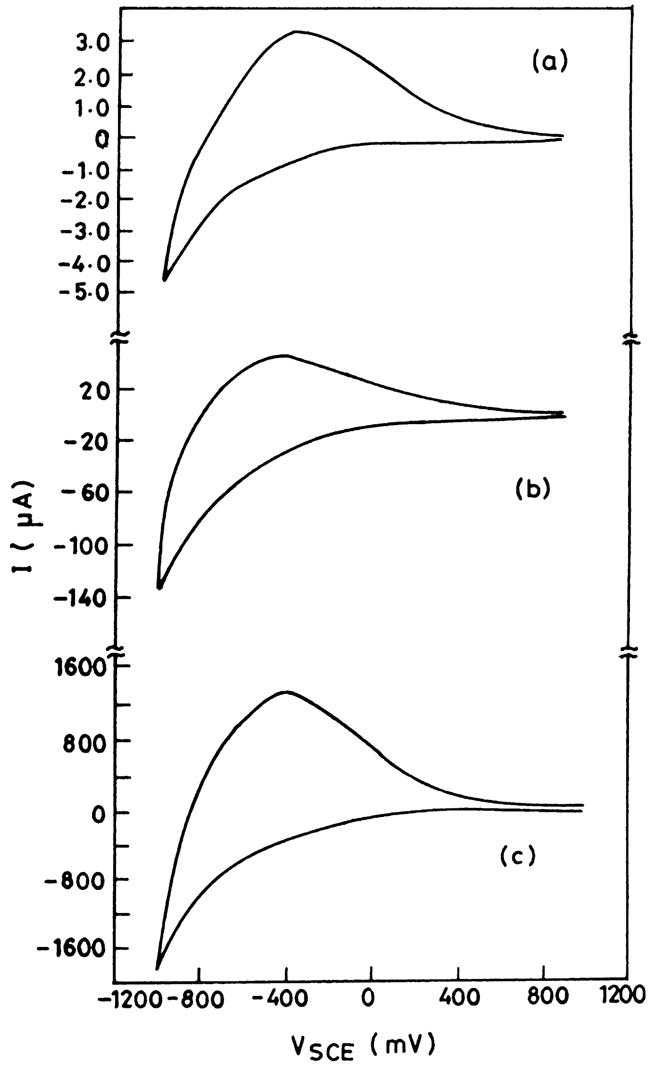

Fig. 2. Cyclic voltammogram for ion intercalated and de-intercalated WO_3 films at (a) 0.1 N (b) 0.5 N (c) 1.0 N of H_2SO_4.

Table 3
Parameters associated with intercalation and de-intercalation of H^+ ions

Concentration	Anodic peak current, I_{pa} (μA)	Cathodic peak current, I_{pc} (μA)	Diffusion co-efficient for I_{pa} (10^{-11} cm^2/s)	Diffusion co-efficeint for I_{pc} (10^{-11} cm^2/s)
0.1 N	0.35	1.40	1.35	2.70
0.5 N	3.20	4.20	0.98	2.08
1.0 N	1400	1900	2.69	3.10

intercalation/de-intercalation. IR absorption variation is related to ion exchange reactions upon immersion of WO_3 films is an important observation which predicts that the alkali ions can replace protons in hydroxyl groups inside the films.

Hence a detailed study of the FT-IR spectra of the as-deposited and the intercalated WO_3 films were recorded. WO_3 films deposited at 0.5 mA/cm^2 were used for this purpose and the intercalation of H^+ ions was done by performing cyclic voltammetry in 0.1, 0.5 and 1.0 N solutions of the H_2SO_4 electrolyte. Fig. 3a shows the FT-IR spectra of the as-deposited WO_3 film which shows a broad peak in the region of 3500–3780 cm^{-1} corresponding to the O–H stretching vibration. This is in accordance with the observation of the O–H broad peak for the WO_3 films prepared by the sol–gel method as reported by Orel et al. [11]. Reichman and Bard [4] have also reported the presence of the broad peak at 3500 cm^{-1} and this peak is assigned due to the presence of water with hydrogen bonding. They have also shown the presence of a sharp peak at 1650 cm^{-1} due to O–H stretching which is observed for the as-electrodeposited WO_3 films in our study.

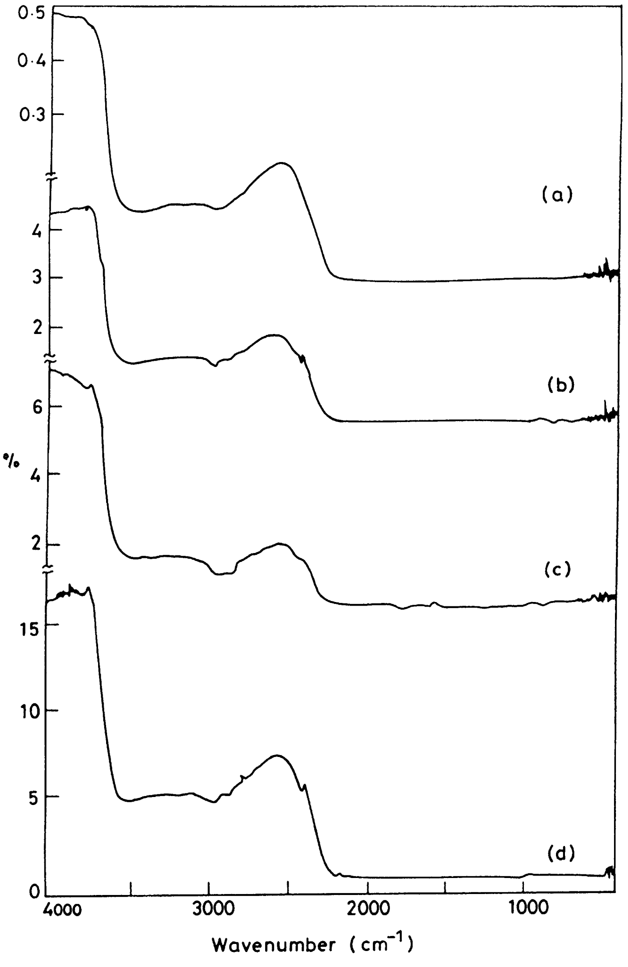

Fig. 3. FT-IR spectra of the WO_3 films (a) before intercalation and intercalated in (b) 0.1 N, (c) 0.5 N and (d) 1.0 N of H_2SO_4.

Fig. 3b, c and d show the FT-IR spectra of the electrodeposited. WO_3 films after intercalation in 0.1, 0.5 and 1.0 N H_2SO_4 electrolyte respectively. The various bands assigned with different frequencies are given in Table 4 for both the WO_3 films studied before and after intercalation. It is evident from the table that different types of bands corresponding to W–O, water and hydroxyl ion are present in the as-electrodeposited film itself. They are about 3400 cm^{-1} for OH–H, about 855 cm^{-1} for W–O–W and 2200 cm^{-1} band for hydroxyl ion. After performing cycling experiments, during which intercalation and de-intercalation takes place, the peak pertaining to W–O–W is observed in the region of 855–835 cm^{-1}. It shows that the electrodeposited WO_3 films are highly stable in H_2SO_4 electrolytes after intercalation. This is comparable to the EC behavior of electron beam evaporated WO_3 film, reported by Yoshiike et al. [14], stored in 0.3 N $LiBF_4$-PC electrolyte at 70 °C for 500 h. But the hydroxyl ion band and water molecule band do not change much as the concentration of H_2SO_4 is changed form 0.1 to 1.0 N.

FT-IR spectrum recorded in the transmittance mode as shown in Fig. 3a of the (WO_3) film deposited at 0.5 mA/cm^2 is showing a broad peak from 3780 to 3500 cm^{-1} which indicates the O–H stretching vibration. Orel et al. [11] have reported the presence of this peak for their WO_3 films prepared by the sol–gel method. Reichman and Bard [4] reported the IR spectra of WO_3 film prepared by the thermal evaporation method showing a broad peak at 1650 and 3500 cm^{-1} which are the characteristic peaks of water molecule. FT-IR spectrum of the WO_3 film deposited, by the electron beam evaporation method and reported by Yosiike et al. [14], on a Si wafer and stored in 0.3 M $LiBF_4$-PC electrolyte at 70 °C, showed a decrease in the intensity of the shoulder of O–H stretching broad peak at 3400 cm^{-1}. This is similar to the behavior of the films in $LiClO_4$-PC

Table 4
Band assignment from the FT-IR spectra of as electrodeposited WO_3 films before and after intercalation in different H_2SO_4 concentration

Band assignment	Before intercalation wave number (cm^{-1})	Wave number (cm^{-1}) (after intercalation)		
		0.1 N	0.5 N	1.0 N
W–O–W corner sharing	674	–	–	–
W–O–W edge sharing	724	–	–	–
W–O–W	855	835	838	814
Hydroxyl	2200	2377	2358	2364
OH–H	3543	3564	3564	3531
Coloration	3758	3749	3737	3749

electrolyte but does not show any change in the intensity of the W–O stretching broad peak at 650 cm^{-1} for both the electrolytes. For the electrolyte of H_2SO_4 (at 0.1, 0.5 and 1.0 N) the peaks are identified for WO_3 films and are shown in Table 4. Fig. 3 shows all the FT-IR diagrams.

In the electrodeposited WO_3 films, the spectra in the transmittance mode shows $\sim$3400 cm^{-1} for OH–H and 855 cm^{-1} for W–O–W and 2200 cm^{-1} band for hydroxyl ion of the film. The IR spectrum reveals the ion injection in the intercalated and de-intercalated WO_3 films. When the intercalation and de-intercalation of the film, there is a decrease in the band from 855 to 835 cm^{-1} for W–O–W but the hydroxyl ion band and water molecule band do not change much as the concentration of the electrolyte changed from 0.1 to 1.0 N.

4. Conclusion

The electrodeposited WO_3 films are thick blue in color, well adherent and uniform. The stochiometric WO_3 shows the polycrystalline nature with triclinic structure. The diffusion co-efficient is varied from 1.0×10^{-11} to 2.69×10^{-11} cm^2/s the ion intercalation and de-intercalation of the films. FTIR-spectra of the electrodeposited WO_3 films show good agreement with the reported values.

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