

## Structural and optical properties of WO<sub>3</sub> electrochromic layers prepared by the sol-gel method

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**Abstract:** Thin layers of tungsten trioxide have been prepared from an aqueous solution of peroxotungstic acid (PTA) using the sol-gel method. Compositional, structural and optical characteristics of WO<sub>3</sub> coated on indium tin oxide (ITO) conductive glass substrates were studied using X-ray diffractometry (XRD), cyclic voltammetry (CV), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Monoclinic and triclinic crystalline structures for thin film and powdered WO<sub>3</sub> were confirmed by XRD analysis. SEM micrograph of annealed samples revealed micro cracks due to a decrease in density and a contraction of layers. EDX analysis showed that 1:2 ratio of oxygen and tungsten atoms in the prepared films is obtained at heat treatment temperatures higher than 200 °C. Furthermore, the annealed samples showed very good electrochromic behavior in cyclic voltammetry studies. Refractive index "n" and extinction coefficient "k" values were found to be reduced by increasing the wavelength and decreasing the temperature.

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### 1 Introduction

In recent years, there has been great interest towards electrochromic applications and device fabrication, such as display panels, electrochromic mirrors and smart windows [1-3].

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The electrochromic phenomenon refers to the application of a low electric field in some transition metal oxides, which causes a new optical absorption band formation by the oxo-redox process and consequently color changes. The reaction is reversible and by removing the electric field, the color of the material is restored [4].

There are several promising electrochromic materials, but among them,  $\text{WO}_3$  due to its high coloration efficiency ( $50 \text{ c/m}^2$ ), quick response time (0.5 s) and long life ( $10^7$  cycles), is of great interest [5]. Many techniques have been reported in the preparation of  $\text{WO}_3$  thin films. Anodic oxidation, sputtering, vacuum deposition and the sol-gel method are common techniques which have been used in research [6,7]. Advantages of the sol-gel method to the other techniques are low cost and simplicity. In addition, the films are obtained at a low heat treatment temperature, and preparation parameters are easily controlled. Additionally, a large area deposition of films from starting materials can be easily achieved. This research employs an aqueous solution of peroxotungstic acid (PTA) for deposition of  $\text{WO}_3$  films, and subsequently investigated its structural, compositional and optical properties.

## 2 Experimental Method

### 2.1 Preparation of peroxotungstic acid (PTA)

Eight grams of Tungsten powder at 99.9 % purity supplied by Merck co. was carefully added to a 25 cc mixture of water and hydrogen peroxide (50:50). Since the reaction is strongly exothermic, an icy ambient was employed. The excess of tungsten powder and hydrogen peroxide were removed by filtration and  $60 \text{ }^\circ\text{C}$  bath ambient, respectively. Subsequently, a pale yellow solution is obtained [8].

A rapid gellation of solution occurred by the blowing of air and the condensation process, which lead to the formation of a yellow solid material. We have noticed that the product is soluble in water and other polar solvents and usable for only a few days at  $10 \text{ }^\circ\text{C}$  (after a few days it turns into an insoluble polymer). The formation of PTA mainly depends on the degree of excess decomposed  $\text{H}_2\text{O}_2$  in the solution, the atmospheric humidity during the condensation process and the condensation rate.

Our investigations on many samples have revealed that the solidification and condensation stages are critical and have to be accurately controlled. Otherwise, the white insoluble powder may be produced which means no sol would be prepared and hence no  $\text{WO}_3$  film deposition would be possible.

### 2.2 $\text{WO}_3$ coating process

The dipping method was employed for the deposition of  $\text{WO}_3$  thin layers. For this purpose, aqueous solutions of 30 % PTA were taken and Indium Tin Oxide (ITO) glass as a substrates were dipped into the solution with a speed of  $1.3 \text{ mm/s}$ . The number of dipping time per sample was four, and calcinations processes of the films were carried out

at different temperatures between 120-500 °C for an hour.

## 2.3 Techniques of analysis

X-ray diffraction patterns (XRD) of the  $\text{WO}_3$  powder and  $\text{WO}_3$  films coated on conducting glass (ITO) were recorded in  $2\theta$  range from 3-60 ° using a Philips PW 1840 diffractometer. A diffracted beam was monochromatized to select  $\text{Cu-K}\alpha$  radiation by a graphite monochromator. Infrared spectra of xerogel were performed by Fourier transform infrared spectroscopy (FT-IR) model Shimadzu 4600. Thermal gravimetric analysis-differential scanning calorimetry (TGA-DSC) curve of xerogel was examined on a Rheometric STA-1500 at a scan rate of 10 °C/m. Electrochemical coloration of the films was studied on a Trace analyzer 746VA in 1M  $\text{H}^+$  under the applied voltage of 1.5 V for 60 S. The transmission spectra of films were recorded on a Carry-17D double beam spectrometer in the range 300-700 nm. The morphology and chemical composition of the films were observed by scanning electron microscopy/energy dispersive X-ray analysis (SEM/ EDAX) Philips XL-30.

## 3 Results and discussion

### 3.1 Characterization of PTA

FT-IR Spectra recorded at a range of 400-4000  $\text{cm}^{-1}$  from PTA showed that stretching vibrations of  $\text{W}(\text{O}_2)$  and  $\text{W-O}$  were occurred at 567  $\text{cm}^{-1}$  and 936  $\text{cm}^{-1}$ .

As Yamanaka et al. have reported, the presence of these peaks indicates the formation of  $[(\text{O}_2)_2\text{W}(\text{O})_2\text{O}]^{2-}$  complex [9].

PTA is a yellow-colored amorphous solid which becomes crystalline after calcination. Our studies on PTA showed the same appearance. A monoclinic structure was obtained for  $\text{WO}_3$  powder after calcinations at 500 °C. Its diffraction pattern is illustrated in Fig. 1.

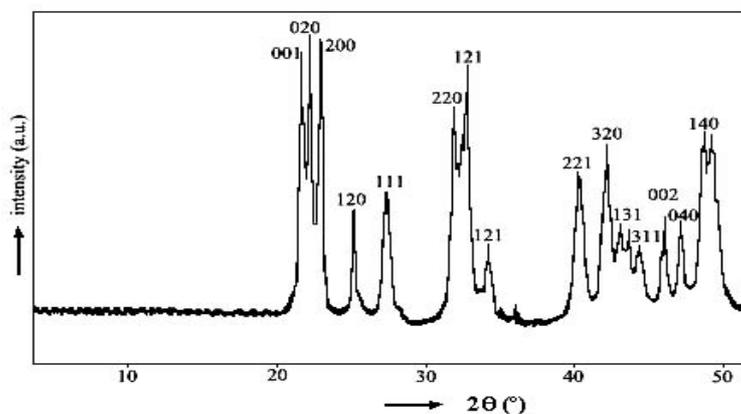


Fig. 1 XRD pattern of  $\text{WO}_3$  powder calcinated at 500 °C.

Differential scanning calorimetry and Thermogravimetric analysis of xerogel (gel dried

under ambient condition) are given in fig 2. The TGA thermogram illustrated an 11 % weight loss at 60-150 °C and a 4 % weight loss at 350 °C. Additionally, the DSC thermogram indicated an occurrence of PTA condensation and polymerization as a result of dehydration and deoxidation at 350 °C. At approximately 380-500 °C, there was a small exothermic peak clearly seen in the DSC thermogram. This peak indicated the onset of  $\text{WO}_3$ .

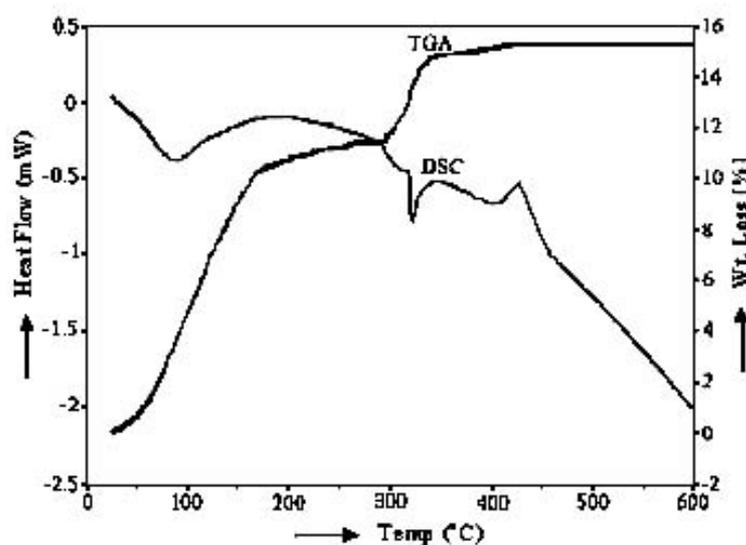


Fig. 2 TGA-DSC patterns of xerogel.

## 3.2 Characterization of the coatings

### 3.2.1 X-ray diffraction pattern

In order to study the crystalline structure of  $\text{WO}_3$  films coated on glass substrates, several specimens prepared under different conditions were examined. The film without any heat treatment (as deposited) and films subjected to annealing temperature from 120-400 °C were found to be amorphous. Whereas, samples heated at 500 °C exhibited triclinic structure. In Fig. 3 an X-ray diffraction pattern of calcinated film at 500 °C is shown. Thus, comparison of XRD results in Fig. 1 and Fig. 3 showed that a new crystalline phase in  $\text{WO}_3$  thin film with triclinic structure (compared to  $\text{WO}_3$  in powder form with monoclinic structure) has grown [10].

### 3.2.2 Electrochromic properties

The electrochromic characterization of  $\text{WO}_3$  coated films was carried out on a cell with the configuration of (ITO /  $\text{WO}_3$  HCL (0.1M) / Pt /SCE). The Potential of the cell was measured with respect to the saturated calomel electrode (SCE) and the platinum was used as a counter electrode. Ionic current of specimens were recorded with 0.1 volts/second scanning speed under +1 volt to - 1 volt applied potential w.r.t. SCE.

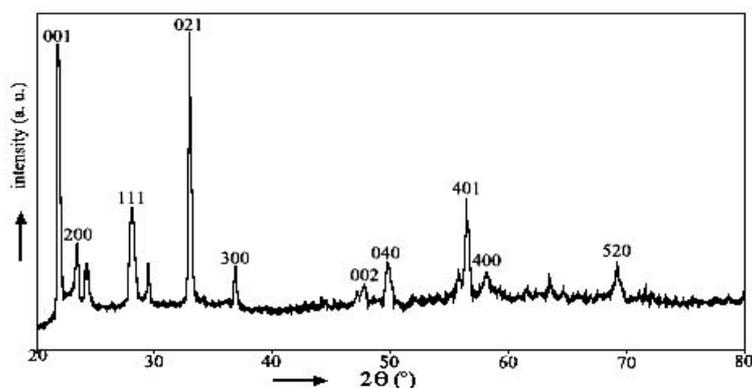


Fig. 3 XRD pattern of  $\text{WO}_3$  film fired at 500 °C.

Fig. 4 shows a voltammogram of  $\text{WO}_3$  thin films annealed between 120–500 °C in air for an hour. The role of the heat treatment on CV performance is interesting at 120 °C. As the amount of heat is not sufficient, PTA is being dissolved in a bath solution and hence, the ion current decreases by a decrease in negative bias, resulting in an insufficient colored species. Similarly, poor coloration-bleaching cycles are also noticed when samples are heated to above 200 °C, particularly at 500 °C as shown in Fig. 4. The ion current reaches its minimum rate. It was concluded that the annealing of  $\text{WO}_3$  films at elevated temperatures leads to denser layers; as a result the permeability of  $\text{H}^+$  ions becomes weak [11]. This means that annealing at 500 °C is not useful. In addition, the films which were heat treated at 200 °C for an hour, exhibited good reversibility, better CV performance and faster  $\text{H}^+$  ions movement. This improvement can be attributed to the polymerization and dehydration of  $\text{WO}_3$  film.

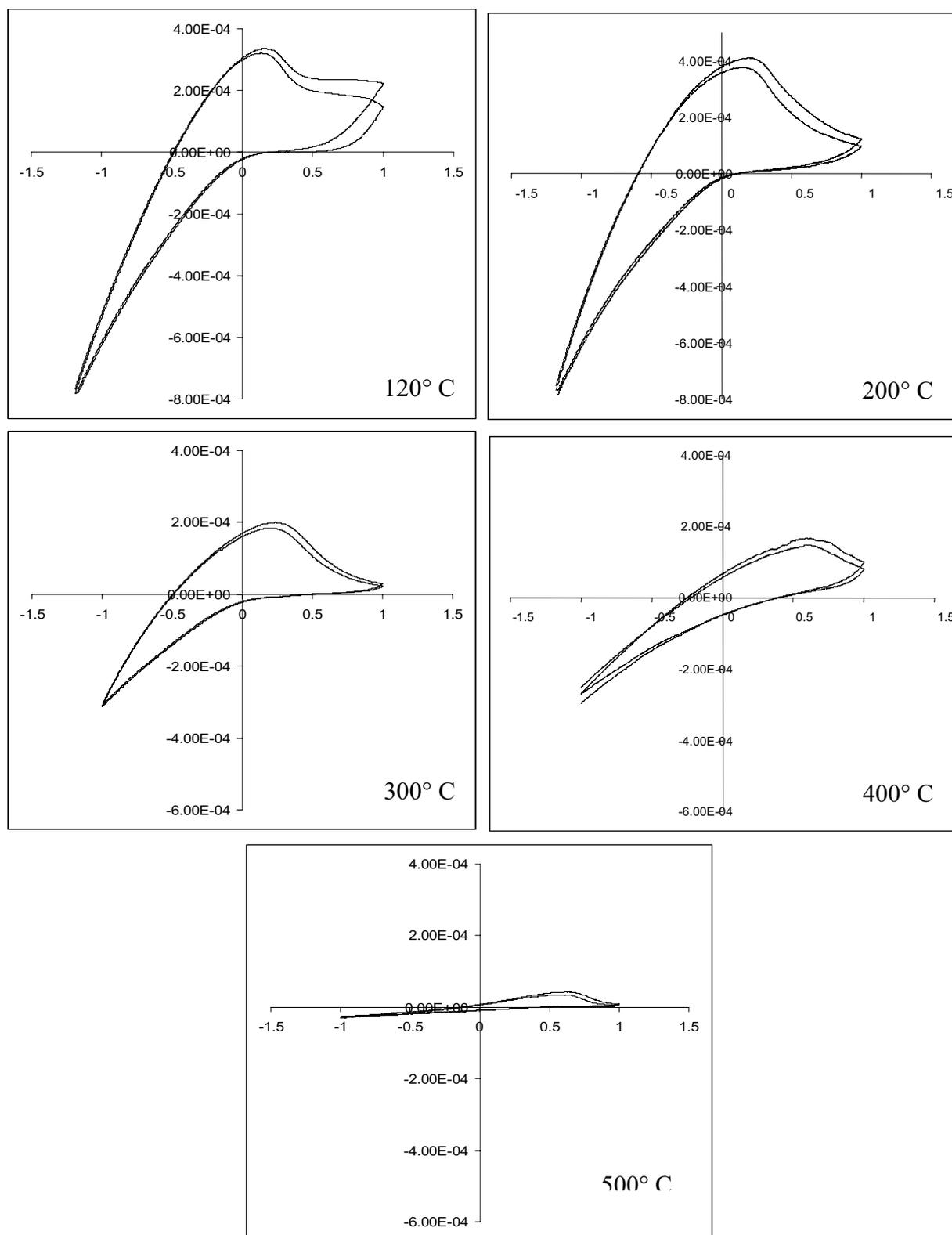
The SEM micrograph of tungsten trioxide film is shown in Fig. 5. Cracks exist on the film texture which is due to the strain imposed on the layer during the heat treatment and the removal of the water (dehydration). Our study revealed that these cracks do not affect the electrochromic properties of the films. Nevertheless, they can be diminished by some organic additives.

### 3.2.3 Optical properties

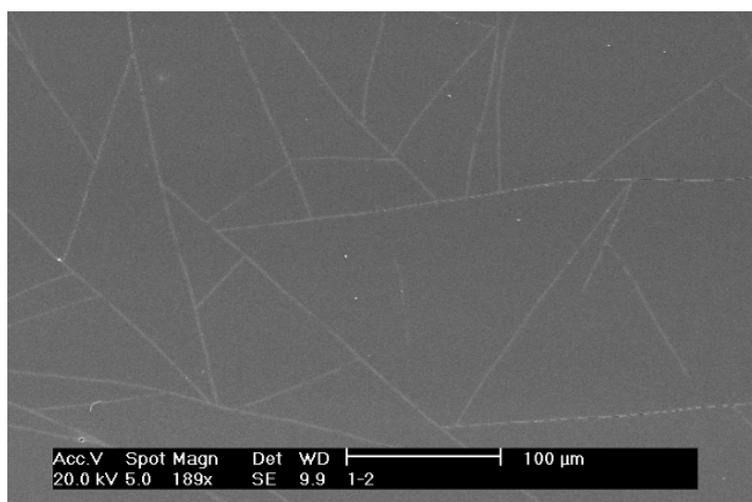
Spectrophotometric transmittance characteristics were studied to determine the optical parameters of  $\text{WO}_3$  thin films annealed at different temperatures. The most important optical parameters which concerned include transmittance (T), refractive index (n), extinction coefficient (k), film thickness (d) and optical transition.

Fig. 6. shows the transmittance spectra of the samples treated by heat at 200, 300 and 500 °C for the wavelength range of 250–700 nm. It is obvious that specimens annealed at 200 °C & 300 °C are about 80 % transparent. At 500 °C, the heat effects lead to the densification of  $\text{WO}_3$ , drastically reducing the transparency.

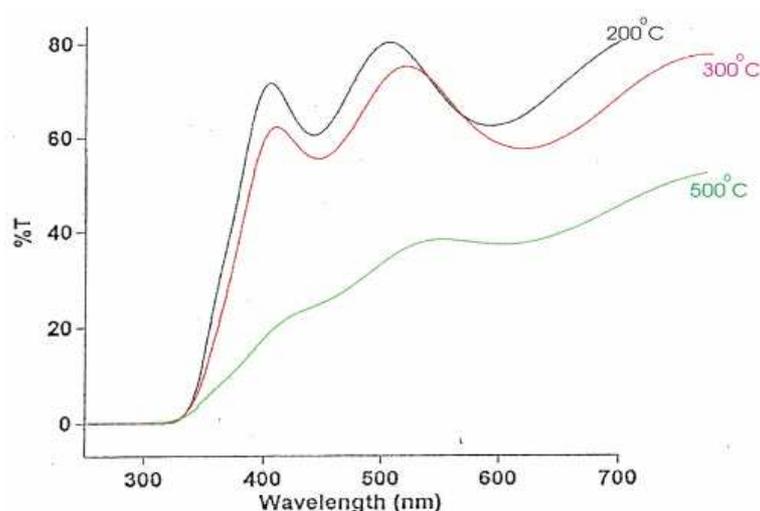
The thickness of the film is also affected by annealing temperatures. It decreased from 250 nm to 150 nm for the samples which were heat treated at 200 °C and 500 °C, respectively. A similar observation has been reported elsewhere [12].



**Fig. 4** Cyclic voltammograms of  $\text{WO}_3$  films on ITO glass electrode in  $1\text{M H}^+$  solution, calcinated at different temperatures.



**Fig. 5** Scanning electron micrograph of  $\text{WO}_3$  film deposited on ITO glass substrate, annealed at 200 °C.

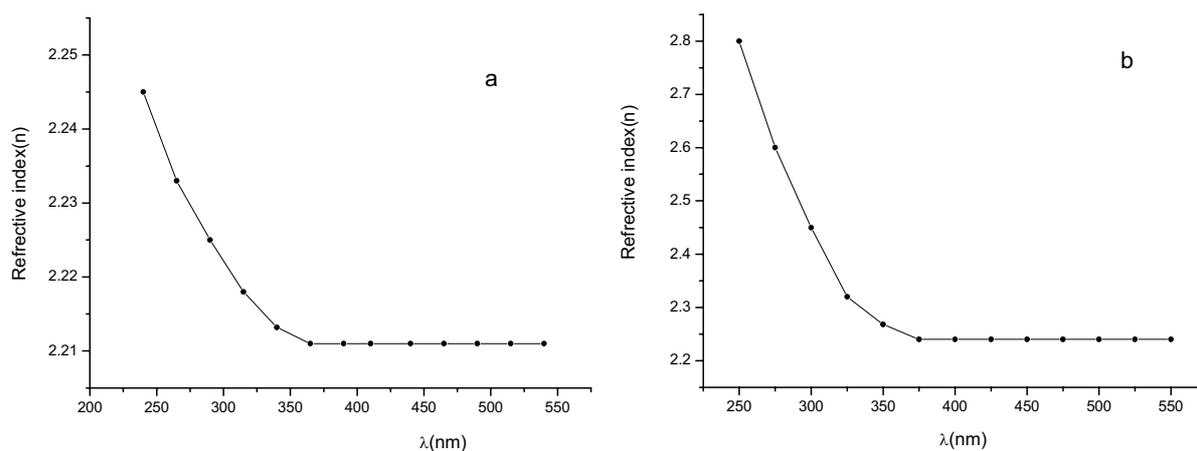


**Fig. 6** Optical transmittances of  $\text{WO}_3$  films, heat treated at different temperatures.

The refractive index of  $\text{WO}_3$  film depends on heat treatment temperature. Figs. 7a and 7b illustrate the variation of the refractive index ( $n$ ) against the incident wavelength ( $\lambda$ ) for typical  $\text{WO}_3$  annealed at 200 °C and 500 °C respectively. Both figures exhibit presence of dispersion and non dispersion regions. The strong dispersion is attributed to the electronic transition from valence band to conduction band. As shown in Figs. 7a,b, maximum dispersion is located at  $\lambda < 360$  nm and  $\lambda < 375$  nm respectively.

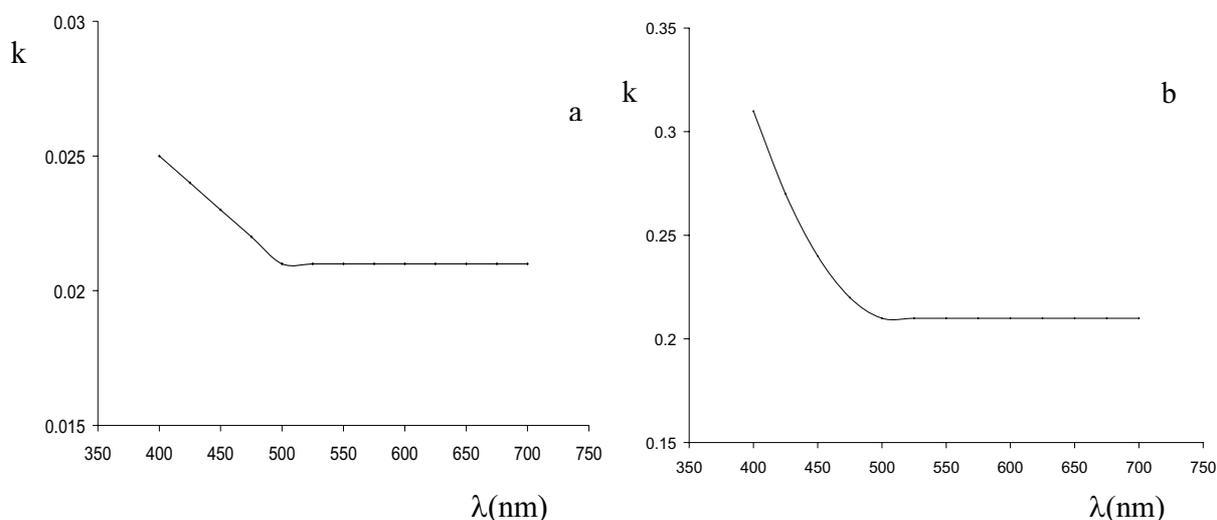
We also observed that the "n" value increases slightly an increase in annealing temperature (i.e. Fig. 7b). A similar increase in refractive index with temperature has also been reported by N. Ozer [13].

As a result of heat treatment, extinction coefficient of  $\text{WO}_3$  films ( $k$ ) shows a similar trend in variation of the refractive index. Fig. 8a. shows the plot of  $k$  (values) vs.  $\lambda$  (wavelength over 350 nm to 700nm) for the specimens annealed at 200 °C & 500 °C, respectively. The behaviors of both plots are the same, but the  $k$  values are different



**Fig. 7** Spectral dependence of the refractive index,  $n$ , of  $\text{WO}_3$  films heat treated at: a) 200 °C; b) 500 °C.

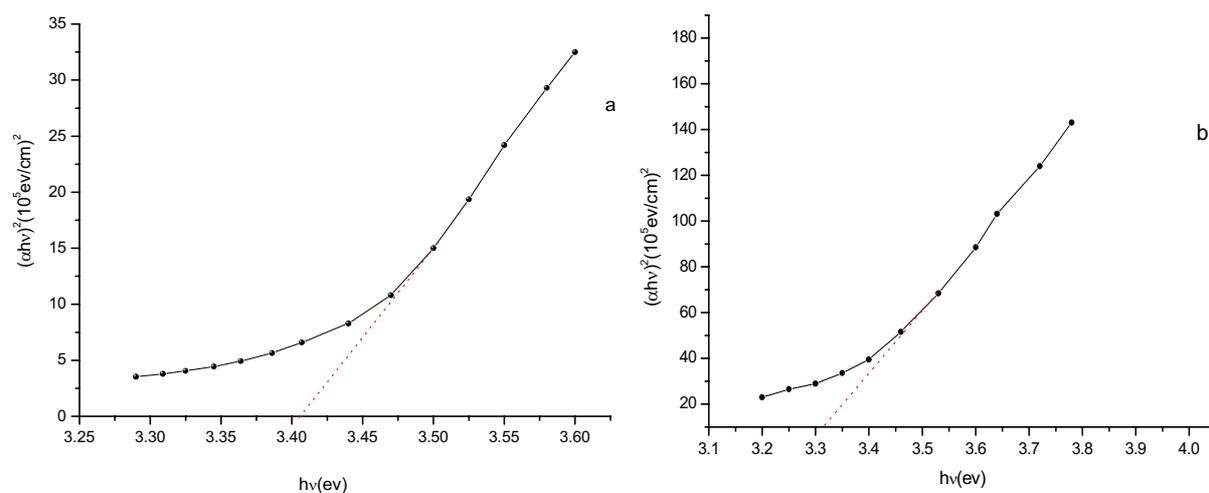
at 500 °C due to high densification and more crystallization. The extinction coefficient varies from 0.025 to 0.02 while for those samples annealed at 200 °C it changes from 0.3 to 0.2. This clearly indicates that in Fig. 8b films are less absorbent and more transparent compared to Fig. 8a it is vice versa.



**Fig. 8** Spectral dependence of the extinction coefficient,  $k$ , of  $\text{WO}_3$  films annealed at: a) 200 °C; b) 500 °C.

Tungsten oxide is known to be an "n" type semiconductor in the crystalline as well as amorphous phases [14]. In order to determine the optical energy gap of the samples, empirical relation  $\alpha h\nu = k(h\nu - E_g)^m$  for near optical absorption in semiconductors were used [15]. Where  $k$  is a constant,  $E_g$  is the band gap,  $\alpha$  is the absorption coefficient of light and proportional to  $\log(1/T)$ . Figs. 9a,b show photon energy dependence of  $(\alpha h\nu)^2$  for the  $\text{WO}_3$  films annealed at 200 °C and 500 °C respectively.

These curves consist of linear portions when extrapolated to  $(\alpha h\nu)^2 = 0$  providing direct



**Fig. 9** Variation of absorption data as a function of photon energy for WO<sub>3</sub> film annealed at: a) 200 °C; b) 500 °C.

inter band transition. These specimens (Figs. 9a,b) exhibited a band gap almost 3.4eV and 3.3eV respectively. Our band gap values are almost similar to the reported value for WO<sub>3</sub> prepared by thermal vacuum evaporation [16] and higher than the films prepared by CVD [17] and spray pyrolysis [18].

Differences between estimated band gap values in different reports are frequently seen. It can be a result of phase transition, strain, imperfection, and excitation effects on the specimens.

## 4 Conclusion

The WO<sub>3</sub> thin films were successfully prepared from PTA aqueous solution as a starting material by the sol-gel technique. The preparation of yellow color solid PTA soluble in water and polar solvents is an important task for this research. The process mainly depends on the rate of dissolution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and the speed of densification. WO<sub>3</sub> films were deposited on ITO glass substrates by dipping the substrate in a 30 % aqueous solution of PTA. The number of dipping times and post deposition annealing were examined. It was revealed that dipping four times at a speed of 1.3 mm/s and 200 °C calcinations temperature is an optimum condition.

FT-IR analysis confirmed the composition of [(O<sub>2</sub>)<sub>2</sub>W(O).O.W(O)(O<sub>2</sub>)<sub>2</sub>]<sup>-2</sup>. Also the X-ray diffraction pattern (XRD) indicated a triclinic crystalline structure for powder tungsten trioxide which was yielded from yellow color solid PTA calcinated up to 500°C.

Thermograms of TGA and DSC analysis showed WO<sub>3</sub> crystallization occurring at approximately 450 °C.

Significant about this research is that the heat treatment has to be controlled. An attempt was made to obtain dense, polymerized and crystalline WO<sub>3</sub> films. Although annealing at elevated temperatures (up to 500 °C) is useful, electrochromic properties

strongly suffer at 500 °C.

The CV plots analysis revealed that annealing at a lower temperature (200 °C) is quite suitable as good reversibility was observed.

The optical parameters such as the refractive index, extinction coefficient and optical band gap were estimated as a function of photon energy. It was found that changes in optical values can only be attributed to a change in the crystalline configuration as a result of heat treatment.

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## References

- [1] N. Sharma, M. Deepa, P. Varshney and S.A. Agnihotry: "Influence of organic additives on the morphological, electrical, and electrochromic properties of sol-gel derived WO<sub>3</sub> coatings", *J. Sol-Gel Sci. & Technol.*, Vol. 18, (2000), pp. 167–173.
- [2] P.K. Varshney, Nidhi, R. Ramachandran and S.A. Agnihotry: "Colloidal tungstic oxide films for electrochromic applications: preliminary studies", *Ind. J. Pure & Appl. Phys.*, Vol. 37, (1999), pp. 262–265.
- [3] T. Nishide and F. Mizkani: "Crystal structures and optical properties of tungsten oxide films prepared by a complexing-agent-assisted sol-gel process", *Thin Solid Films*, Vol. 259, (1995), pp. 212–217.
- [4] Y.V. Renard, G. Leveque, A. Abdellaoui and A. Donnadiou: "Optical constants of electrochromic polycrystalline WO<sub>3</sub> thin films prepared by chemical vapor deposition", *Thin Solid Films*, Vol. 203, (1991), pp. 33–39.
- [5] H. Keneko and K. Miyake: "Estimation of the composition parameter of electrochemically colored amorphous hydrogen tungsten oxide films", *J. Appl. Phys.*, Vol. 66, (1989), pp. 845–850.
- [6] G. Lrftheriotis, S. Papaefthimiou, P. Yianoulis and A. Siokou: "Effect of tungsten oxidation states in the thermal coloration and bleaching of amorphous WO<sub>3</sub> films", *Thin Solid Films*, Vol. 384, (2001), pp. 298–306.
- [7] K.D. Lee: "Preparation and electrochromic properties of WO<sub>3</sub> coating deposition by the sol-gel method", *Sol. Energy Mater & Sol. Cells*, Vol. 57, (1999), pp. 21–30.
- [8] R.R. Amachandran, Nidhi, S.A. Paradeep and S.A. Agnihotry: "Sol-gel deposition of EC-WO<sub>3</sub> films using a precursor with enhanced stability", *Ind. J. Pure & Appl. Phys.*, Vol. 37, (1999), pp. 353–355.
- [9] K. Yamanaka, H. Oakamoto and H. Kidou: "Peroxtungstic acid coated films for electrochromic display devises", *Jpn. J. Appl. Phys.*, Vol. 25, (1986), pp. 1420–1426.
- [10] Joint Committee on Powder Diffraction Standard: Powder Diffraction File, PA. Swarthmore. 1972, Card Nos. 2-310, 5-363.

- [11] K.D. Lee: “Deposition of  $\text{WO}_3$  thin films by the sol-gel method”, *Thin Solid Films*, Vol. 302, (1997), pp. 84–88.
- [12] H.L. Hartnagel, A.L. Dawar, A.K. Jain and C. Jagadish: *Semi conducting Transparent Thin Films*, IOP, London, 1995.
- [13] N. Ozer: “Optical and electrochemical characteristics of sol-gel deposition tungsten oxide films: a comparison”, *Thin Solid Films*, Vol. 304, (1997), pp. 310–314.
- [14] I. Shimizu, M. Shizukuishi and E. Inoue: “Solid state electrochromic devices consisting of amorphous  $\text{WO}_3$  and  $\text{Cr}_2\text{O}_3$ ”, *J. Appl. Phys.*, Vol. 50, (1979), pp. 4027–4032.
- [15] T. S. Moss: *Optical Properties of Semiconductors*, Butter Worth, London, 1961.
- [16] H. Demiryont and K. Nietering: “Tungsten oxide films by reactive and conventional evaporation techniques”, *Appl. Opt.*, Vol. 28, (1989), pp. 1494–1498.
- [17] A. Dannadieu, D. Davazoglou and A. Abdelloui: “Structure, optical and electro-optical properties of polycrystalline  $\text{WO}_3$  and  $\text{MoO}_3$  thin film prepared by chemical vapor deposition”, *Thin Solid Films*, Vol. 164, (1988), pp. 333–338.
- [18] P.R. Patil and P.S. Patil: “Preparation of mixed oxide  $\text{MoO}_3$ - $\text{WO}_3$  thin films by spray pyrolysis techniques and their characterization”, *Thin Solid Films*, Vol. 382, (2001), pp. 13–22.