Preparation and Characterization of WO_3 Electrochromic Films Obtained by the Sol-Gel Process

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ABSTRACT: *Tungsten trioxide (WO_3) films have been coated on indium thin oxide (ITO) conductive glass substrate, using aqueous solution of peroxotungstic acid (PTA) by the sol-gel dip coating method. X-ray diffractometery (XRD) analysis confirmed monoclinic and triclinic structure for the film and powdered WO_3 respectively. Fourier transforms infrared spectroscopy (FT-IR) exhibited the structure of peroxotungstic acid. The SEM micrograph of annealed species revealed micro cracks due to decrease of density and contraction of layers. Energy- dispersive X-ray (EDX) study determined 1:3 ratios of oxygen and tungsten atoms in the prepared films at heat treatment temperature higher than 200ºC. The electrochromical behavior was investigated in 1M HCL solution employing cyclic voltammetry. It was found that WO_3 films demonstrated good reversibility at 200 ºC.*

KEY WORDS: *Sol-gel, Tungsten oxide, Thin film, Electrochromic, Coating.*

INTRODUCTION

In recent years, there has been great interest towards electrochromic applications and device fabrication, such as display panels, electrochrom mirrors and smart windows [1-3]. 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, WO_3 due to its high coloration efficiency (50 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 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 WO_3 films, and subsequently investigated its structural and electrochromic properties.

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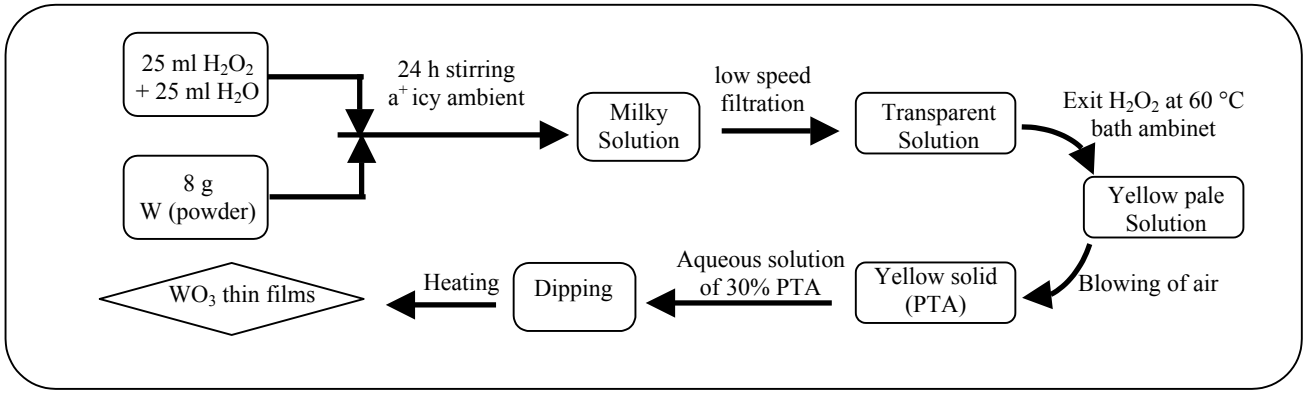

Fig. 1: The various films processing steps in WO_3 preparation.

EXPERIMENTAL PROCEDURE

The film processing stages of WO_3 is given in Fig. 1, and details of each process are described as following:

Preparation of peroxotungstic acid (PTA)

Eight grams of Tungsten powder at 99.9% purity supplied by Merck Co. was carefully added to a 50 ml mixture of water and hydrogen peroxide (50:50). Since the reaction is strongly exothermic, an icy ambient was employed. After a few hours the milky solution of WO_3 was obtained and then filtered to remove the excess of tungsten powder, giving transparent solution. Also, to remove the excess of H_2O_2, it was heated at 60 °C, by this way a deep yellow solution was yielded. Finally, the solution was rapidly condensed in air blowing at room temperature leading a yellow glassy crystal of PTA (as shown in Fig. 1) [8].

We have noticed that the product is soluble in water and other polar solvents and usable for only a few days at 10 °C (after a few days it turns into an insoluble polymer). The formation of PTA mainly depends on the degree of excess decomposed H_2O_2 in the solution, the atmospheric humidity during the condensation process and the condensation rate [9].

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 WO_3 film deposition would be possible.

WO_3 coating process

The dipping method was employed for the deposition of WO_3 thin layers. For this purpose, aqueous solutions of 30% PTA were taken and Indium Tin oxide (ITO) glass as a substrates (with dimension of: 3×2 cm^2) were dipped into the solution with a speed of 1.3 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.

Techniques of analysis

X-ray diffraction patterns (XRD) of the WO_3 powder and WO_3 films coated on conducting glass (ITO) were recorded in 2θ range from 3-60° using a Philips PW 1840 diffractometer. A diffracted beam was monochromatized to select Cu-Kα 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 Rheometeric STA-1500 at a scan rate of 10°C/m. Electrochemical coloration of the films was studied on a Trace analyzer 746VA in 1M H^+ under the applied voltage of 1.5 V for 60 S. The morphology and chemical composition of the films were observed by scanning electron microscopy/energy dispersive X-ray analysis (SEM/ EDAX) Philips XL-30.

RESULTS AND DISCUSSION

Characterization of PTA

FT-IR Spectra recorded at a range of 400-4000 cm^{-1} from PTA showed that stretching vibrations of $W(O_2)$ and W-O were occurred at 567cm^{-1} and 963cm^{-1} (Fig. 2).

As Yamanaka et al. have reported, the presence of

these peaks indicates the formation of $[(O_2)_2W\ (O).O.W\ (O)\ (O_2)_2]^{2-}$ complex [9].

PTA is a yellow-colored amorphous solid which becomes crystalline after calcinations. Our studies on PTA showed the same appearance. A monoclinic structure was obtained for WO_3 powder after calcinations at 500ºC. Its diffraction pattern is illustrated in Fig. 3.

Differential scanning calorimetry and Thermo-gravimetric analysis of xerogel (gel dried under ambient condition) are given in Fig. 4. 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 350ºC. At approximately 380-500 ºC, there was a small exothermic peak clearly seen in the DSC thermogram. This peak indicated the onset of WO_3.

Characterization of the coatings

X-ray diffraction pattern

In order to study the crystalline structure of 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 120-400ºC were found to be amorphous. Whereas, samples heated at 500ºC exhibited triclinic structure. In Fig. 5 an X-ray diffraction pattern of calcinated film at 500ºC is shown. Thus, comparison of XRD results in Fig. 3 and Fig. 5 showed that a new crystalline phase in WO_3 thin film with triclinic structure (compared to WO_3 in powder form with monoclinic structure) has grown [10].

Electrochromic properties

The electrochromic characterization of WO_3 coated films was carried out on a cell with the configuration of (ITO / 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. 6. shows a voltammogram of WO_3 thin films annealed between 120-500 ºC in air for an hour. The role of the heat treatment on CV performance is interesting at 120 ºC. As the amount of heat is not sufficient, PTA is

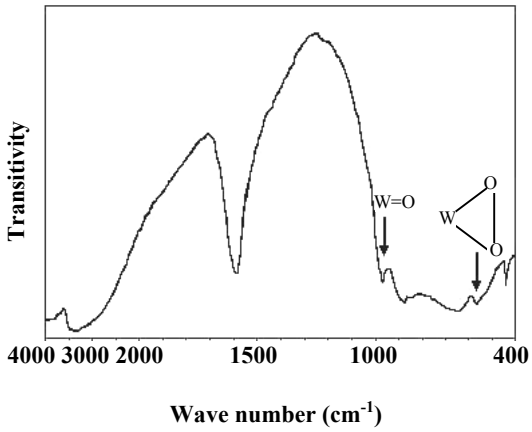

Fig. 2: FT-IR Spectra for WO_3 film (KBr tablet).

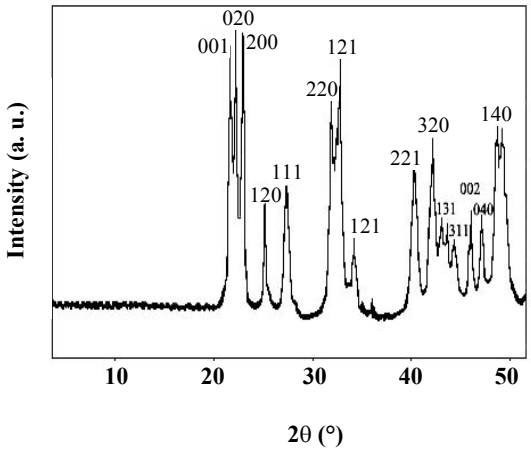

Fig. 3: XRD pattern of WO_3 powder calcinated at 500 ºC.

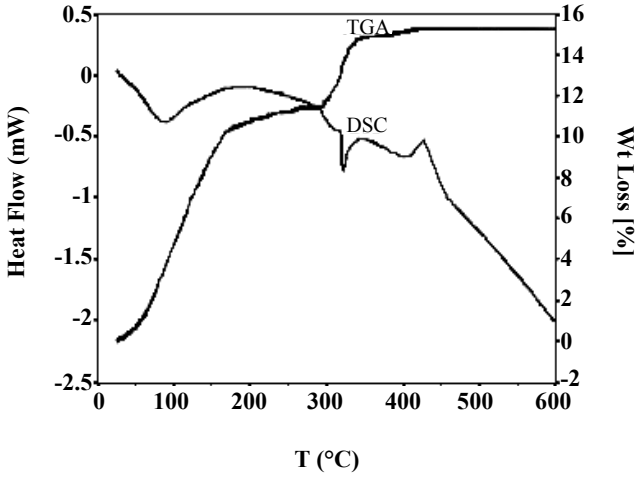

Fig. 4: TGA-DSC patterns of xerogel.

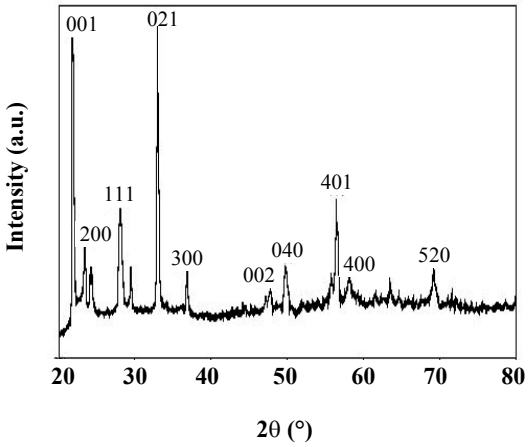

Fig. 5. XRD pattern of WO_3 film fired at 500 ºC.

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 200ºC, particularly at 500ºC as shown in Fig. 6. The ion current reaches its minimum rate. It was concluded that the annealing of WO_3 films at elevated temperatures leads to denser layers; as a result the permeability of H^+ ions becomes weak [11]. This means that annealing at 500ºC is not useful. In addition, the films which were heat treated at 200ºC for an hour, exhibited good reversibility, better CV performance and faster H^+ ions movement. This improvement can be attributed to the polymerization and dehydration of WO_3 film.

The SEM micrograph of tungsten trioxide film is shown in Fig. 7. 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.

CONCLUSIONS

The WO_3 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_2O_2) and the speed of densification. WO_3 films were deposited on ITO glass

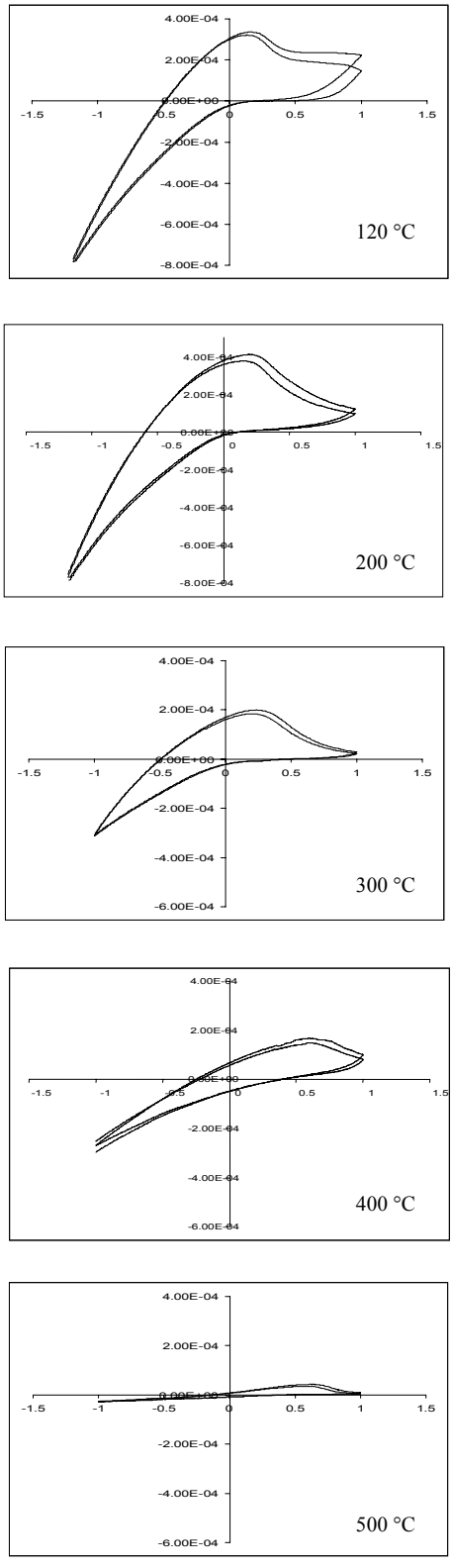

Fig. 6: Cyclic voltammograms of WO_3 films on ITO glass electrode in 1M H^+ solution, fired at different temperatures.

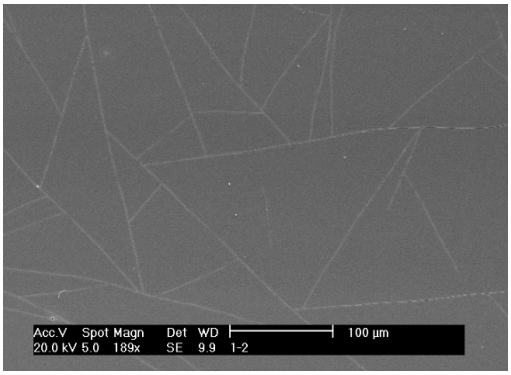

Fig. 7: Scanning electron micrograph of WO_3 film deposited on ITO glass substrate, annealed at 200ºC.

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 200ºC calcinations temperature is an optimum condition.

FT-IR analysis confirmed the composition of $[(O_2)_2W(O).O.W(O)(O_2)_2]^{-2}$. 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 500ºC.

Thermograms of TGA and DSC analysis showed WO_3 crystallization occurring at approximately 450 ºC.

Significant about this research is that the heat treatment has to be controlled. An attempt was made to obtain dense, polymerized and crystalline WO_3 films. Although annealing at elevated temperatures (up to 500 ºC) is useful, electrochromic properties strongly suffer at 500ºC.

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

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