Characterization of WO₃ Thin Films Prepared at Different Deposition Currents on CTO Substrates

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INTRODUCTION

An electrochromic window popularly called “smart window” shows dynamically variable light transmission characteristics under external bias. This feature may be effectively used to control penetration of solar radiation into buildings, automobile interiors etc. Potential advantages offered by electrochromics include a long-term open circuit memory and a low power requirement. The possible use of both organic and inorganic electrochromic materials in such windows has been extensively studied. Among the inorganic materials, WO₃ has received much attention due to its potential use as a battery electrode and also as a complementary electrode in smart windows and electrochromic (EC) systems. In such materials, an optical change can be reversibly introduced upon double injection of positive ions and electrons leading to colouring and bleaching (colourless).

EXPERIMENTAL

A stock solution was prepared by dissolving 2 g of tungsten powder in 20% of hydrogen peroxide and adding few drops of H₂SO₄ until the effervescence ceased. Conducting transparent oxide (CTO) coated glass substrates at about 10Ω/cm² sheet resistance, cleaned ultrasonically in triple distilled water.
were used as cathode for galvanostatic deposition. A platinum electrode was used as counterelectrode and a standard calomel electrode as reference electrode. Unless otherwise stated, all the potentials are referred to $V_{SCE}$. Deposition was carried out using EG&G PAR 362 potentiostat for 30 min to 120 min at a current density of 0.50, 0.65, 0.75 mA/cm$^2$. The deposition parameters like temperature of the bath, pH of the electrolyte, concentration of the electrolyte were optimized to obtain well adherent, uniform and pinhole free colorless films. The structure of the films was identified by powder X-ray diffraction using JEOL JDX803a X-ray diffractometer with CuKα radiation in the $2\theta$ range 20 to 80°. The X-ray generator was operated at 40 KV and 20 mA. The scanning speed employed was 0.5°/min for recording the diffractograms. To have an idea about the surface elemental composition of the film, energy dispersive analysis by X-rays (EDAX) was carried out using Philips EDX spectrometer (XL30 ESEMTEM).

The surface morphology of the electrodeposited WO$_3$ films were analyzed by JEOL JSM 6400 instrument. Optical absorption, transmittance and reflectance spectra were recorded in the normal incidence mode from 300 to 1400 nm using UV-Vis-NIR spectrophotometer (SHIMADZU 2410S). FT-IR spectra were recorded between 2000 cm$^{-1}$ and 400 cm$^{-1}$ in transmittance mode using JASCO CANVAS 460 PLUS spectrophotometer.

RESULTS AND DISCUSSIONS

XRD Structural Study

WO$_3$ films deposited at current densities of 0.50, 0.65 and 0.75 mA/cm$^2$ were analyzed by using the X-ray diffraction technique. The XRD spectrum of the film is shown in Figure 1 and the $d$-values are compared with the reported values [JCPDS 20-1323] as shown in Table 1. The sharp peaks confirm the polycrystalline nature of the WO$_3$ films deposited at all current densities. The presence of the peaks corresponding to the planes (022) and (202) with $d$ values of 2.62 and 2.76 Å respectively are the characteristic XRD peaks revealing their triclinic structure. The crystallite size was calculated from the full width at half maximum (FWHM) of the XRD peaks and found to be in the order of 0.6 μm. The lattice parameters of the film deposited at 0.50 mA/cm$^2$ are $a = 7.511$ Å, $b = 7.689$ Å and $c = 7.311$ Å. The diffraction peaks observed for the asdeposited films in the present study at $2\theta = 26.8°$ and 45.30° are similar to that reported by Shutcher and Guygen [10] for the thermally evaporated film.

The XRD diffractogram for the deposition current density 0.65 mA/cm$^2$ shows the characteristic feature of triclinic system, i.e., the characteristics pair of peaks show reduced peak intensity and the preferential orientation peak also show variation with respect to WO$_3$ films deposited at 0.50 mA/cm$^2$. The XRD for the films deposited at a current density of 0.75 mA/cm$^2$, does not show the characteristic pair of peaks.

Reichmann and Bard [11] reported that the WO$_3$ film prepared by thermal oxidation of W in air shows pair of peaks at 2.64 Å and 2.66 Å is the characteristic property of the triclinic structure. Scalfani et al. [12] reported that the peak at $2\theta = 39.9°$ is attributable to bare WO$_3$ with triclinic structure prepared by the catalysis route. In the present work, though the electrodeposited WO$_3$ thin film show slight variation from the reported values of the miller plane (002) but still exhibits the triclinic nature of the thin film. Maruyama and Arai [13] reported that the film deposited by the chemical vapor deposition technique at 400°C show $d$ values for (222) and (002) planes, indicating that the film is composed of crystallites with triclinic structure. The diffraction pattern of the stochiometric WO$_3$ intrinsic film prepared by pulse

FIG. 1. XRD Pattern WO$_3$ thin film for 0.50, 0.65 and 0.75 mA/cm$^2$. 

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TABLE 1
Comparison of d values with JCPDS

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<th>d (Å)</th>
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<tr>
<td></td>
<td>Observed</td>
</tr>
<tr>
<td>3.324</td>
<td>(1 2 0)</td>
</tr>
<tr>
<td>2.891</td>
<td>(1 1 2)</td>
</tr>
<tr>
<td>2.769</td>
<td>(0 2 2)</td>
</tr>
<tr>
<td>2.627</td>
<td>(2 0 2)</td>
</tr>
<tr>
<td>2.36</td>
<td>(2 2 2)</td>
</tr>
<tr>
<td>2.08</td>
<td>(2 0 3)</td>
</tr>
</tbody>
</table>

electrodeposition as reported by Yu et al.\[^{14}\] belong to the triclinic system. Hutchins et al.\[^{15}\] (1998) reported that the peak at 2θ = 30° is due to the WO₃ prepared by electrochemical deposition. Similarly Bragg peak is observed at 2θ = 30.9° in the present work for the electrodeposited film at current density 0.50 mA/cm².

The comparison of d values reported by Machido and Enyo\[^{16}\] for RF sputtered WO₃ films after intercalation; the electrocolouration of WO₃ is attributed to the formation of hydroxyl type hydrogen bronze. This observation also explains the electrochromic property in WO₃·2H₂O is independent of the structure of the films produced by the RF sputtering method. This indicates that the electrocolouration is not due to the formation of oxygen vacancy but due to the insertion of H⁺ ions into the WO₃ lattice.

**EDAX Study**

The surface composition of WO₃ films were analyzed by taking EDAX spectrum. The spectra taken in the energy range between 0.3 and 9.3 KeV for the films deposited on CTO substrates at current densities 0.50, 0.65 and 0.75 mA/cm² as shown in Figures 2(a–c), respectively. From the spectrum, it was found that the weight percentage of elements present is about 26% of Tungsten and 74% of oxygen in the electrodeposited film deposited at 0.50 mA/cm². The ratio of the weight percentage of W and O is nearly three, approaching the near stochiometry of WO₃ for the films deposited at the optimized condition keeping the current density at 0.50 mA/cm². But for the deposition current density of 0.65 mA/cm², the ratio of the weight percentage of W and O is nearly 1:2.46 and for the current density 0.75 mA/cm², the ratio of the weight percentage of W and O is nearly 1:2.72. The stochiometric ratio of all the deposition current is slightly less than the stochiometric WO₃ films deposited at 0.50 mA/cm².

**SEM Study**

The SEM photograph of the electrodeposited WO₃ thin films shows well adherent and uniform surface morphology without any visible cracks and pinholes. Figure 3 shows the surface morphology of the WO₃ thin film, which exhibits platelets of uniform spherical size spread all over the surface, deposited at a current density of 0.50 mA/cm². This resembles the surface morphology reported by Yu et al.\[^{14}\] for WO₃ film deposited by pulsed electrodeposition route, and also similar to the films deposited by the pulsed laser ablation technique and catalysis technique.\[^{12,17}\] The SEM micrographs of the films deposited at 0.65 and 0.75 mA/cm² exhibit pentagon like platelets with some free space in between the two pentagon platelets. It reveals that the deposition of stochiometric and device quality WO₃ films is dependent on the current density in the electrodeposition technique.
Optical Studies

Development of semiconducting oxide materials with controllable energy gap is necessary for the increased applications in liquid crystal display and optoelectronic devices. Hence the absorption and transmission properties were studied to calculate the band gap variations. The expected variation of $\alpha$ with photon energy for absorption $E_g$ is given by $\hbar \omega \alpha = K (\hbar \omega - E_g)^n$ where $K$ is essentially a constant, $E_g$ is the band gap and $n$ is a constant, which can be assigned the values of $1/2$, $3/2$ and $2$ for the allowed indirect transition, forbidden direct transition and allowed indirect transition, respectively. Optical absorption and transmittance spectra were taken in the normal incidence mode from 300 to 1400 nm using UV-Vis–NIR spectrophotometer. The optical absorption spectrum of the WO$_3$ film predicts that this compound absorbs fewer amounts of photons in the lower energy region and due to this low absorption, multiple interference effect is predominant. Maximum transmittance about 80% and reflectance about 70% in the respective spectrums are observed for the electrodeposited tungsten trioxide film. Figures 4 and 5 represent the absorption and transmittance spectrum respectively of the WO$_3$ film. Figure 6 shows the reflectance spectrum of the films deposited at various current densities. A graph is drawn between $\hbar \omega$ and $(\hbar \omega)^{1/2}$ and the linear portion of the graph is extrapolated such as to cut the energy axis as shown in Figure 6. This gives an indirect band gap of 3.2 eV and agrees well with the reported value of the 3.2 eV for the WO$_3$ film prepared by photochemical vapor deposition technique.

The optical band gap of the electrodeposited tungsten trioxide film for the current at 0.65 and 0.75 mA is calculated and found to be 2.9 eV and 2.5 eV, respectively. Takayo Kubo and Yoshinori Nishikitani reported that the optical band gap values converging to a constant value between 2.8 and 2.7 eV are assigned to crystalline WO$_3$ films. The observed band gap values of our films are in good agreement with band gap 2.9 eV of the WO$_3$ films prepared by chemical vapour deposition technique. Optical transmittance of WO$_3$ film of 450 nm thickness varies from 80% to 40% in the visible region. The optical properties and the absorption coefficient value are similar to that reported for the WO$_3$ deposited by DC magnetron sputtering technique.

The refractive index and the extinction coefficient values vary from 1.9 to 2.9 and from 0.01 to 0.08 respectively for the current density of 0.50 mA/cm$^2$ as shown in Figure 7. The corresponding values for the WO$_3$ films deposited at 0.65 and 0.75 mA/cm$^2$, are found slightly deviating from the reported values. These values are comparable to the reported...
values of Bader et al.\cite{21} for their WO$_3$ films prepared by the thermal evaporation method. The reflectance spectra of WO$_3$ films showed significant variation in the infrared region which coincides with the behaviour as reported for the sputtering deposited WO$_3$ film.\cite{22,23}

### FT-IR Study

FT-IR spectra of WO$_3$ films, electrodeposited at different current densities is shown in Figure 8 and the vibrational band assignment and frequencies in cm$^{-1}$ are given in Table 2. The film deposited at 0.50 mA/cm$^2$ shows peaks (Figure 8a) at 657, 724 and 855 cm$^{-1}$ are assigned to stretching vibration of W–O bond corresponding to well-grown crystalline phase. This confirms the XRD results of our films as discussed earlier that the films deposited at 0.50 mA/cm$^2$ are well crystallized and belong to a triclinic system. There are broad peaks centered 2200 and 3500 cm$^{-1}$ indicating O-H stretching vibration and water molecule. Figures 8b and 8c show the IR spectra of WO$_3$ films deposited at 0.65 and 0.75 mA/cm$^2$ respectively where the low frequency lines are absent.

#### TABLE 2

<table>
<thead>
<tr>
<th>Absorption band (cm$^{-1}$)</th>
<th>Band assignment</th>
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<tr>
<td>0.50 mA/cm$^2$</td>
<td>0.65 mA/cm$^2$</td>
</tr>
<tr>
<td>657</td>
<td>—</td>
</tr>
<tr>
<td>724</td>
<td>—</td>
</tr>
<tr>
<td>855</td>
<td>801</td>
</tr>
<tr>
<td>2200</td>
<td>2535</td>
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<td>3543</td>
<td>3503</td>
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<tr>
<td>3758</td>
<td>3772</td>
</tr>
</tbody>
</table>

Oral et al.\cite{6} reported IR peaks corresponding to polycrystalline WO$_3$ films prepared by the sol-gel method. Benjamin Reichman and Bard\cite{11} 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 is the characteristic
peaks of water molecule. FT-IR spectrum of the WO₃ film, deposited by the electron beam evaporation technique[24] on a Si wafer and stored in 0.3 M LiBF₄-PC electrolyte, showed decreased intensity for the shoulder of O–H stretching broad peak at 3400 cm⁻¹ while W–O stretching broad peak at 650 cm⁻¹ remain unchanged. These results reveal that the vibrations related to O–H mode and water molecules are invariably present in WO₃ films prepared by all the reported techniques.

CONCLUSIONS

WO₃ films have been galvanostatically electrodeposited on CTO glass substrate from aqueous solution containing tungsten powder mixed with the hydrogen peroxide. Polycrystalline nature of the film with triclinic structure and lattice parameters values has been determined, which agrees well with the data for 0.50 mA/cm². The surface elemental compositional analysis of the film by EDAX shows the near stoichiometry for the deposition current density of 0.50 mA/cm². The ratio between the W and O for the current densities 0.65 and 0.75 mA/cm² does not obey stiochiometry. The XRD analysis show that the crystalline structure is triclinic. The SEM photograph for the deposition current density 0.50 mA/cm² of the film shows the device quality nature of the surface without any pinholes. The transmittance spectrum showed high transmission of the smart window and for the reflectance also. Optical measurements revealed indirect band gap of value 3.2 eV. FT-IR spectra of the electrodeposited WO₃ films show good agreement with the reported values.

REFERENCES