Morphological, optical and electrochromic properties of dry-lithiated nanostructured WO₃ thin films

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Tungsten trioxide (WO₃) thin films were prepared by thermal evaporation technique on thoroughly cleaned glass substrates at high pressure of 133.322 mPa in presence of argon. The substrate temperature was maintained from 6 °C to 8 °C with the help of a cold jar. The deposited films were annealed at 400 °C in air for about 2 hours. The films were characterized in terms of their composition by X-ray photoelectron spectroscopy. Subsequently, the laboratory developed dry lithiation method was used to intercalate lithium atoms into as-deposited films in various proportions. With the amount of lithium content inserted into the film, the films showed coloration in visible and near infrared regions. The morphology, coloration efficiency and optical constants of annealed and lithiated films were calculated.

Keywords: WO3 thin films; thermal evaporation; XPS; atomic force microscopy; optical and electrochromic properties

1. Introduction

Among transition metal oxides, for example, vanadium pentoxide (V₂O₅), molybdenum trioxide (MoO_3) and tungsten trioxide (WO_3) , the researchers have expanded their consideration towards WO₃ because of its high stability, wide bandgap, high coloration efficiency and relatively low cost. Moreover, WO₃ has distinct physical and chemical properties [1, 2] that make it suitable for electrochromic devices, selective catalyst for oxidation and reduction reactions [3-6], environmental monitoring, gas sensing devices [7–10], transparent conducting electrodes, optical smart windows, display devices [11-14]. The combination of these solid state materials with thin film technology has significantly reduced the size of the devices and hence, improved the efficiency of the devices for various scientific and technological applications. WO₃ thin films show coloration in both amorphous as well as crystalline states due to absorption and reflectance modulation, respectively [1] under certain electrochemical conditions. This property allows WO₃ for its practical applications, such as energy saving windows, solar roofing, antiglare

rear-view mirrors or advertising panels [15, 16]. Electrochromism is a property of a material whose color is changed reversibly by the direction of an applied electromotive force. These materials have received considerable attention both in science and industry owing to their optical modulation in visible or infrared region [17–19]. To explain the phenomenon of electrochromism of WO₃, a lot of theoretical models were proposed based on its electronic structure. The formation of tungsten bronze is the basis for electrochromism. The bronze is formed by the double injection of an electron from an electrode and a charge compensating ion from the electrolyte into the interstitial sites of tungsten oxide [20]. The reversible process in WO₃ can be represented as:

$$WO_3 + xM^+ + xe^- \iff M_x WO_3 (0 \le x \le 1)$$
 (1)

There are two important factors which can influence the electrochromism of a material. The first factor is a time constant of the intercalation reaction which is controlled by diffusion coefficient and length of the diffusion path [21]. The second factor, which controls the electrochromic properties such as coloration efficiency, cyclic durability and kinetics of coloration to the bleaching process of the films is the crystal structure of the grown films.

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In turn, the composition of the grown films, structure, morphology and grain size strongly depend on the deposition technique and the deposition parameters. Nowadays, nanostructured thin films have attracted much higher attention than bulk materials due to the large fraction of surface atoms and strong surface adsorption. Various deposition techniques are employed to deposit WO₃ thin films including thermal evaporation, pulsed laser ablation, sputtering, electron beam evaporation, anodic oxidation, spray pyrolysis, sol-gel and electrodeposition [22–25]. By varying the deposition parameters in the chosen technique one can deposit nanostructured films. In the present investigation, the films were deposited by thermal evaporation technique which is an industrially practiced method for large area substrates. In this technique, the material can be evaporated by either resistive heating or radio frequency heating. In this work, the morphology, optical properties and coloration efficiency of dry lithiated films have been studied at different lithiation levels.

2. Experimental

Thin films of WO₃ were deposited on chemically and ultrasonically cleaned corning 7059 glass substrates by thermal evaporation technique. The substrates were cleaned thoroughly by ultrasonic agitation in methanol then in acetone and after that washed with deionized water. Next, the substrates were allowed to dry in a clean, hot air oven. After that, the substrates were degassed prior to the film deposition. Pure WO₃ (99.99 %) powder, obtained from Sigma Aldrich & Co., was put in the electrically heated molybdenum boat in required proportions. The deposition was carried out in a chamber initially evacuated to a base pressure of 133.322 µPa and backfilled with pure argon gas to higher pressures (133.322 mPa). The well-cleaned substrates were placed on a substrate holder with suitable masks in a bell jar and the substrate holder was covered by a shutter. The distance between the source and substrate was maintained at 14 cm during the deposition. The substrates were cooled below room temperature (6 °C to 8 °C) with water circulated in cold finger. After getting the desired vacuum, in the presence of argon gas, the boat was slowly heated. When the temperature of the boat reached to nearly 1567 °C, the shutter was opened and the deposition was started by maintaining the boat at the same temperature. The thickness of the films was found to be 200 nm by maintaining the deposition rate as 0.2 nm/s which was measured approximately by using a built-in quartz crystal thickness monitor. After deposition, the films were subjected to thermal treatment with a filament heater at 400 °C for about 2 hours. The composition of the experimental films was studied by using X-ray photoelectron spectroscope (XPS) SECA 2200i-XL. The morphology of WO₃ films was determined by using atomic force microscopy (AFM) Digital Instruments (Dimension 2300) in tapping mode. UV-Vis double beam spectrophotometer UV-1800 Shimadzu was used for measuring the optical transmission spectra of the films in the wavelength range of 300 nm to 2400 nm. Subsequent to the characterization of deposited films, small amount of lithium (2.5 nm, 5.0 nm, 7.5 nm, 10 nm and 12.5 nm) was inserted into the samples by laboratory developed dry lithiation method [25]. Transmission spectra of lithiated films were also taken and the optical bandgap values were evaluated. By comparing the transmittance of bleached and colored states, the coloration efficiency of the films with respect to charge insertion was calculated. The coloration efficiency CE is defined as:

$$CE = \Delta OD/Q$$
 (2)

where the optical density change is calculated by taking the logarithmic ratio between the transmission of the film in the "as-deposited" T_b and colored T_c states:

$$\Delta OD = \log(T_b/T_c) \tag{3}$$

The transmission and reflection photoellipsometry method was used to find the optical constantsrefractive index n and extinction coefficient k in the wavelength range of 300 nm to 800 nm [26, 27].

3. Results and discussion

Fig. 1 shows the X-ray photoelectron spectra of WO_3 thin films deposited at a high



Fig. 1. XPS spectra of annealed WO₃ thin films (a) curves of W (4f), (b) core level spectrum of O (1s).

pressure of 133.322 mPa under argon gas and annealed at 400 °C for about 2 h. These deposition conditions promote the granulation of the film in the vapor phase and hence lead to nanostructured films. The post-deposition annealing was carried out to increase the intergranular contact. The presence of carbon C(1s) peak was observed at about 284.5 eV which was due to atmospheric

contamination or the sample handling prior to XPS measurements (not shown in the figure). The spectra show characteristic doublet $4f_{7/2}$ and $4f_{5/2}$ which is caused by spin orbit splitting in WO₃. The core level binding energies corresponding to $4f_{7/2}$ and $4f_{5/2}$ are found to be of 35.84 eV and 37.99 eV, respectively (shown in Fig. 1a) and O(1s) level at 530.62 eV (shown in Fig. 1b.). Fig. 1b also shows O(1s) at 531.24 eV attributed to O⁻ ions on the subsurface interacting with the W ions, and O (1s) peak at 532.42 eV which is due to subsurface contamination. The 4f peaks are attributed to the fully oxidized tungsten ions (W^{6+}) . The 4f doublet lines are separated by 2.15 eV. The peak positions and energy separations are in a good agreement with the data of WO₃ powder in literature, which suggests that the deposited films have nominal stoichiometry [28, 29]. In addition to the doublet, the less intense peak is observed at 42.01 eV which confirms the presence of $W5p_{3/2}$ state of W, which is partially filled with lower valence states, i.e. W^{+5} . As the intensity of this peak is very low, the oxygen deficiency is minimal and experimental films are stoichiometric [30, 31]. Binding energies and full width and half maximum (FWHM) values for W and O core levels are shown in Table 1.

The AFM images of annealed WO₃ thin films as a function of inserted lithium quantity are shown in Fig. 2. The images clearly show the presence of nanostructure in the films. The as-deposited films after annealing were found to be fairly homogeneous with a mean particle size around 40 nm to 50 nm. It was also observed that there is a slight heterogeneous mix of grains which form irregular clusters. The lithium insertion seems to render the grain size more uniform through reorganization of the internal structure [32]. With the increasing lithium insertion it is seen that the film reorganizes itself giving a larger particle size and a less granular appearance to the film (observable in 12.5 nm thickness of lithium insertion).

Fig. 3 represents the optical transmission spectra of annealed WO₃ thin films with the insertion of (a) 0.0 nm (b) 2.5 nm (c) 5.0 nm (d) 7.5 nm (e) 10.0 nm and (f) 12.5 nm of lithium. The optical transmission changes occur-

| Name | Start BE | Peak BE | End BE | Height counts | FWHM [eV] | Area (P) CPS[eV] |
|---------------------------------|----------|---------|--------|---------------|-----------|---------------------|
| W4f7, 6 ⁺ | 46.33 | 35.84 | 31.86 | 239519.1 | 1.36 | 381956.7 |
| W4f5, 6 ⁺ | 46.33 | 37.99 | 31.86 | 179639.3 | 1.36 | 286467.5 |
| W5p3, 6 ⁺ | 46.33 | 42.01 | 31.86 | 8572.26 | 2.02 | 18436.79 |
| O1s, O ²⁻ | 535.56 | 530.62 | 526.48 | 185213.4 | 1.2 | 270218.4 |
| O1s, subsurface, O ⁻ | 535.56 | 531.24 | 526.48 | 124172 | 1.2 | 181161.6 |
| O1s, surface contamination | 535.56 | 532.42 | 526.48 | 14192.37 | 1.2 | 20706.07 |

Table 1. Binding energies and FWHM values for W and O core levels.





Fig. 2. Atomic force micrographs of annealed WO₃ films with the insertion of (a) 0.0 nm, (b) 2.5 nm, (c) 5.0 nm, (d) 7.5 nm, (e) 10.0 nm, and (f) 12.5 nm lithium.

ring in the films due to the insertion of lithium are clearly observed in Fig. 3. The films were found to be weakly absorbing due to their high transmission values. A sharp decrease in the transmission at a wavelength of about 400 nm corresponds to the fundamental absorption edge. It was also found that the experimental films before lithiation had insignificant broadband absorption. With the insertion of lithium, the absorption edge slightly shifted to higher wavelengths and broad band absorption was observed at around 900 nm. The broad band modulation could be either a combination

of absorption and reflection modulations or a reflection modulation spread out due to the different size and orientation of the grains. The strong suppression of the film interference was observed, which might be due to its uniform granular structure. In the annealed film, the transmission is nearly flat throughout the major part of the spectral region, thus presenting a highly transparent and neutrally colored film. The granular structure which leads to a considerable roughness between the film interfaces breaks the coherence of the light reflected from the two interfaces thus maximizing the transmission.



Fig. 3. Transmission spectra of annealed WO₃ thin films with the insertion of (a) 0.0 nm, (b) 2.5 nm, (c) 5.0 nm, (d) 7.5 nm, (e) 10.0 nm, and (f) 12.5 nm lithium.

Depending on the grain size, the film is prone to a slightly cloudy or milky appearance due to the enhanced diffuse reflectance from the rough surface, especially in angular viewing. As the films are showing high transmittance, hence, the films have low diffuse reflectance.

The lithium insertion renders the film highly colored. The maximum coloration is centered at the wavelength of 1200 nm. The coloration at higher wavelengths is also quite effective [33]. This indicates that the absorption modulation is more dominant than the reflectance. The optical changes in the visible region are fairly insignificant compared to the rest of the spectrum.

The optical absorption coefficient was calculated from the relation [34]:

$$\alpha = 1/t \ln[T/(1-R)^2]$$
 (4)

where α is the absorption coefficient, t is thickness of the deposited film, R is reflectance and T is amount of transmission.

The optical energy band gap of the films was determined from the transmission spectra by using Tauc relation [35, 36] given by:

$$(\alpha h \upsilon) = \beta (h\upsilon - Eg)^n \tag{5}$$



Fig. 4. Optical bandgap of annealed WO₃ thin films with the insertion of (a) 0.0 nm, (b) 2.5 nm, (c) 5.0 nm, (d) 7.5 nm, (e) 10.0 nm, and (f) 12.5 nm lithium.

where hv is the incident photon energy, β is the edge width parameter and n is the exponent value to determine the type of transition. The exponent can take values 1/2, 3/2, 2 and 3 which correspond to direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [37]. The optical data for the as-deposited and lithiated films gave the best fit for the value of exponent n = 2 representing the indirect allowed transitions [38, 39].

Fig. 4 shows $(\alpha h v)^{1/2}$ versus hv plots for the above mentioned WO₃ thin films. The optical bandgap value was found to be about 3.0 eV for annealed WO₃ thin film. With the insertion of lithium, the bandgap values have diminished within the range from 2.98 eV to 2.88 eV, which led to coloration i.e., the formation of Lix WO₃. An effective coloration takes place in the near infrared region, but only to a small extent in the visible region of the spectrum it is observed with increasing lithium insertion. Hence, the films exhibit highly selective coloration. Coloration efficiency of WO₃ film with the insertion of 2.5 nm, 5.0 nm, 7.5 nm, 10.0 nm and 12.5 nm of lithium thickness are shown in Fig. 5. The peak efficiency for 2.5 nm and 12.5 nm of lithium insertion are 208 cm²/C (1291 nm) and 73 cm^2/C (1164 nm), respectively, for the given wavelengths.



Fig. 5. Coloration efficiency of annealed WO₃ thin films with the insertion of 2.5 nm, 5.0 nm, 7.5 nm, 10.0 nm, and 12.5 nm lithium.



Fig. 6. Optical constants refractive index n and extinction coefficient k of annealed WO₃ thin films with the insertion of (a) 0.0 nm (b) 2.5 nm (c) 5.0 nm (d) 7.5 nm (e) 10.0 nm and (f) 12.5 nm lithium in the wavelength region of 300 nm to 800 nm.

The optical indices, refractive index n and extinction coefficient k were calculated by ellipsometry analysis in the wavelength region of 300 nm to 800 nm. Fig. 6 shows the optical constants n and k of annealed WO₃ thin films with the insertion of (a) 0.0 nm, (b) 2.5 nm, (c) 5.0 nm, (d) 7.5 nm, (e) 10.0 nm, and (f) 12.5 nm of lithium thickness. As the films were found to be nanostructured from structural analysis, the thickness of the film was found to be large due to its porous structure [40]. Due to the granular structure of the films, the light transmission is higher than the reflectance. Especially in the nanostructured electrochromic films, it is

a daunting task to discern the reflection and absorption modulations and the lack of coherence has been projected between the reflections from the grains. The refractive index value changes from 1.7 to 2.2 and the k values are found to be less. As the lithium is inserted into the sample there is an insignificant change in the refractive index values and a minute change is observed in the k values at higher wavelengths. These films have higher diffusion and show more disorder. These results are inconsistent with the other reported optical constants of WO₃ thin films [27, 41].

4. Conclusions

Nanostructured WO₃ thin films were prepared by thermal evaporation technique. The composition, morphology and optical properties were discussed. The films were found to be stoichiometric by XPS studies and their nanostructure with grain size of about 40 nm to 50 nm was confirmed by AFM images. The films were lithiated by inserting different amounts of lithium by dry lithiation method. The significant changes in color, grain size and coloration efficiency values were observed which were dependent on the amount of tungsten trioxide present in the film.

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