Abstract

The WO₃ thin films coated on various substrates such as soda-lime glass (SLG), ZnO/SLG and ITO/SLG were prepared using thermal evaporation. Pure WO₃ powder was evaporated and/or was sublimated via a box heater (uniform-flux type) under a high vacuum level of 4x10⁻⁶ mbar. The average deposition rate of 12 nm/min was regulated during the growth process. All as-grown WO₃ thin films were characterized by UV-Vis-NIR spectrophotometer, AFM and XRD for its optical transmission.
morphological and structural properties, respectively. The WO₃ coated soda-lime glass shows high optical transmittance of 85% in the wavelength range of 300 to 2600 nm and the calculated optical band gap of 3.24 eV under an indirect allowed transition. The XRD and AFM images revealed that all WO₃ thin films show poor crystallinity (amorphous-like) and small crystallite size which correspond to the film formation under low temperature. In this work, all amorphous-like WO₃ films show electrochromic properties. The color state (deep blue) was obtained using applied voltage of 2.5V. The different of transmittance between bleach state and color state was 55% at wavelength of 550 nm. The preliminary results suggested that the evaporated WO₃ films with small crystallite size or poor crystallinity gains more surface area of WO₃ to react with the electrolyte solution which needed in the electrochromic layer for smart window devices.

Key Words: tungsten oxide, electrochromic, smart window

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Introduction

Tungsten oxide, WO₃, a wide band gap semiconductor transition-metal oxide, have been studied intensively due to their interesting properties such as electrochromism, photochromism, gas sorption and catalysis. Amorphous tungsten oxide (α-WO₃) thin film was discovered to have the electrochromic property, i.e., to change its color from transparent to blue, reversibly, upon electron injection. Electrochromic devices have many applications such as optical smart windows, display devices and gas sensors.

Fig. 1 shows one of the structure of electrochromic device. It consists of multilayer stack embedded between two transparent conducting oxide (TCO) coated glass substrates. In this structure, the metal oxide films or electrochromic films function as working electrodes. Between two pieces of these substrates is the layer of electrolyte solution which serves as ion storage. When a voltage of the
order of few volts is applied between the transparent electrodes, ions can be exchanged between the ion storage film and the electrochromic film.

![Fig. 1. A schematic of a typical electrochromic device.]

The WO$_3$ films have been prepared by several techniques. Mostly, vacuum-coating processes such as sputtering (Tien-Syh Yang et al., 2005), evaporation (T. Tesfamichael et al., 2007), pulsed laser deposition (R. K. Gupta et al., 2008) or chemical vapor deposition are used to prepare thin layers with thickness of about 400 nm (Andreas. Georg et al., 2008), but other processes like sol-gel, dip-coating (M. Deepa et al., 2006) and spray pyrolysis are also possible. Each technique provides different advantages depending on the type of device, properties of films and cost.

The electrochromism of WO$_3$ thin films has been studied more than 20 years, but it is not clear. The color change in the electrochromic films is believed to be directly related to the double injection and extraction of electron and ions via applied voltage. WO$_3$ film in a bleach state ($W^{6+}$) can be switched to a color state ($W^{5+}$) by insertion of ions and electrons from electrolyte to WO$_3$ films according to the reaction (Se-Hee Lee et al., 1999)

$$\text{WO}_3 + xM^{+} + xe^{-} \leftrightarrow M\text{WO}_3$$  \hspace{1cm} (1)

\begin{align*}
&\text{($W^{6+}$ bleach)} \\
&\text{($W^{5+}$ color)}
\end{align*}

where $M^{+}$ is H$^+$, Li$^+$, Na$^+$, or K$^+$ ions.

Coloration efficiency between bleaching and coloring is directly related to a highly disorder of WO$_3$ films (amorphous-like) (M. H. Francombe et al., 1993). The relatively small crystallite size gains more surface area of WO$_3$ to react with the electrolyte solution.

For an electrochromic devices, mainly smart windows, high optical transmittance of the metal oxide layer and amorphous like properties are important. The aim of this present work is to investigate
the influence of the type of substrates on the optical and morphological properties of WO₃ films grown by thermal evaporation.

**Experimental**

The tungsten oxide films used in this study were prepared on three types of substrates: bared soda-lime glass (SLG) with area of 30x30x2 mm, and indium-tin oxide (ITO) coated on SLG (ITO/SLG) with area of 30x30x3 mm. The films were deposited by conventional thermal evaporation of WO₃ powder (purity 99% Aldrich). The deposition conditions are electrical power of 2 kVA dc power supply, the heater type of Molybdenum box (uniform-flux type), vacuum level of 4x10⁻⁶ mbar, deposition rate of 12nm/min (using *in situ* quartz crystal monitor) and the heater to substrate distance of 12 cm. The structural characterization of as-grown WO₃ films was performed using X-ray diffraction (XRD). The XRD spectra of all films were recorded with Bruker AXS D8 X-ray diffractometer using the θ-2θ scan with CuKα (λ=1.5405 Å). The morphology of films were investigated using atomic force microscope (AFM). The AFM imaging was performed under ambient conditions using a Digital Instruments (Veeco) Dimension 3100 unit with Nanoscope® controller, operated in tapping mode. The optical transmittance measurements were using UV-Vis-NIR photospectrometer (Lambda900).

The electrochemical measurements were carried out in a transparent cell as shown in Fig 2. This cell contains 0.1 M hydrochrolic acid (HCl) as electrolyte, an ITO-coated glass as the counter electrode, the WO₃ grown on an ITO-coated glass as the working electrode. In this report, the bleach state is defined as the applied dc voltage setting at 0 V and the coloring state is the applied dc voltage setting at 2.5 V. Before measuring the optical properties, the transparency of the electrochemical cell without the working electrode was measured as baseline.

![Fig. 2. (a) Schematic and (b) image of the apparatus to evaluate the electrochemical measurements.](image)
Results and Discussion

Structural Properties

Fig. 3 shows the XRD patterns of WO$_3$ films deposited on various substrates. No WO$_3$-XRD peaks observed in WO$_3$ grown on substrates. It is suggested that the films structure is amorphous, which means that if there are crystallites their sizes are rather small beyond the measurement sensitivity. The presence of amorphous phase in films is in good agreement with many research groups reported that Raman spectra of as-grown WO$_3$ films shows broad features.

Fig. 3. X-ray diffraction patterns of WO$_3$ films on (a) SLG, (b) ZnO/SLG and (c) ITO/SLG.

Morphology Investigations

The surface morphology of WO$_3$ deposited on bared SLG, ZnO/SLG and ITO/SLG was investigated with AFM as shown in Fig. 4a-c. AFM images of WO$_3$/SLG and WO$_3$/ZnO/SLG substrates show smooth surface, small grain size which indicates the amorphous nature of the films. The large grain size of the films was found in WO$_3$/ITO/SLG film which can be implied that the improvement in crystallite size of the film occurs by the coalescence of neighboring nanometer crystallites size during deposition process. The surface roughness was calculated from the AFM scans and is shown in Table 1. The porosity of the films was found to decrease with increasing crystallinity of substrates. Comparison between WO$_3$ grown on SLG and on ZnO/SLG shows that the quality of WO$_3$/ZnO/SLG film surfaces was improved, lower porosity, larger cluster’s diameter. For WO$_3$/ITO/SLG clusters with diameter larger than 0.1 $\mu$m appeared on the film surface. The change in surface morphology with type
of substrate may be due to the different surface energy leading to crystallites of varying crystalline nature and size.

![AFM images](image1)

**Table 1:** Surface roughness of tungsten oxide film deposited on various substrates, determined from AFM scans.

<table>
<thead>
<tr>
<th>Type of substrate</th>
<th>Root mean square roughness (nm)</th>
</tr>
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<tbody>
<tr>
<td>Bared SLG</td>
<td>1.35</td>
</tr>
<tr>
<td>ZnO/SLG</td>
<td>1.86</td>
</tr>
<tr>
<td>ITO/SLG</td>
<td>20.81</td>
</tr>
</tbody>
</table>

**Optical Properties**

Spectral optical transmittance of WO$_3$ films was measured in the wavelength range of 300 nm to 2600 nm are shown in Fig. 5. As can be seen from the spectra, WO$_3$/SLG has high transmittance in the
visible light range of about 85%. The WO$_3$/ZnO/SLG and WO$_3$/ITO/SLG show low transmittance in the infrared resulting from high infrared absorption of ITO and ZnO. This clearly shows the transparent nature of the film. The optical band gap (E$_g$) of WO$_3$ thin films were calculated using well known Tauc’s relationship. The calculated E$_g$ of WO$_3$ is 3.24 eV. It has been reported that the band gap of WO$_3$ powder produced by oxidation of tungsten powder is approximately 3.25 eV.

![Fig. 5](image)

Fig. 5. Optical transmittance spectra of WO$_3$ deposited on SLG, ZnO/SLG and ITO/SLG.

During electrochemical measurements, the gradual color change from transparent or bleach state at applied voltage of 0 V to slightly blue then to deep blue or color state at applied voltage of 2.5 V. The typical optical transmittance spectra of samples measured for colored (2.5 V) and bleached (0 V) states are shown in Fig. 6. It is apparent that the WO$_3$ film-coated on ITO/SLG shows the large optical modulation in the spectrum range of 300-2600 nm. The samples show deeper color and considerable transmittance difference in the visible spectrum range, with a maximum value of $\Delta T=55\%$ at $\lambda=550$ nm.

![Fig. 6](image)

Fig. 6. Optical transmittance spectra for colored (2.5V) and bleached (0 V) states.
Conclusions

Thin films of WO₃ were deposited by thermal evaporation technique on SLG, ZnO/SLG and ITO/SLG substrates at the room temperature. The influence of substrates on the structural, surface and optical properties of the films is studied. The structural studies reveal that the films structure have amorphous-like nature. The AFM scan results revealed that the small round-like grains are observed in the films grown on SLG and ZnO/SLG, which also confirm the amorphous nature of the films. The optical transmittance spectra shows that the optical band gap of WO₃/SLG films is 3.24 eV corresponding to the highly disordered WO₃ films. Judging from the preliminary results, the WO₃-coated on ZnO/SLG shows high optical transmittance with sharp absorption edge, nanometer crystallite size, high surface-to-volume ratio, which are desirable for electrochromic device applications.

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References


