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RF reactive sputtering of tungsten oxide thin films for application in electrochromic devices

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This research was focused on the electrochromic behaviour of RF-sputtered thin films of tungsten trioxide (WO_3). These thin films, which exhibit cathodic coloration under lithium ion/electron double injection, have a fairly high mixed ion-electron conductivity. Films of various thickness were deposited on conductive glass. The method of reactive sputtering of a tungsten target in the presence of oxygen as the reactive gas was used. The influence of the technological conditions during deposition, and the consequent thermal treatment have been studied. The technological parameters were optimized to obtain films of good optical quality. Using Raman spectroscopy to studying the vibrational properties, the films' crystalline modifications and chemical bonds have been identified. VIS-UV spectrophotometry showed high visible transmittance of the RF-sputtered WO_3 films, which could assure good initial transparency of an electrochromic device, using WO_3 as the functional layer. The films have also been characterized by ellipsometric analysis, using multiangle four zone null ellipsometry. The purpose of the research is the investigation of the structure and electrochromic behaviour of WO_3 thin films. Electrochromic experiments were done and the films showed reversible coloration upon Li intercalation.

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1. Introduction

Tungsten oxide, in a thin film form, is widely investigated as a gas sensor. The operation of most gas sensors is based on the reversible changes of the resistivity of specific materials, caused by the presence of a gas in the environment. Tungsten trioxide (WO_3) has an appreciable sensing capability for gases such as CO, NOx and NH_3. Tungsten oxide films allow easy insertion of organic compounds in their crystal, and this leads to their use in electronic devices and heterogeneous catalysts. Tungsten oxides are particularly attractive technologically, due to their high electronic mobility and high lithium-ion mobility, as well as a low-energy barrier for Li insertion and extraction reactions.

WO_3 films are interesting with respect to their chromogenic, as they exhibit electrochromic, thermochromic and photochromic effects [1]. Electrochromism in amorphous tungsten oxide films has been extensively studied since it was discovered in 1969 [2]. WO_3 thin films, which exhibit cathodic colouration under lithium ion/electron double injection, have a fairly high mixed ion-electron conductivity. Their basic application is in the so-called "smart windows", which are able to switch between two basic modes - a fully transparent state to a coloured state. If applied in solar architectural buildings, such windows control the energy of the solar flux entering the building. Another significant application is in electrochromic displays - a very promising cost-effective technology for large-area displays [1].

The EC, in the case of tungsten oxide, is suggested to be explained as follows:

$$WO_3 + xe- + xM+ \leftrightarrow MxWO_3,$$

where M^+ can be H^+, Li^+, Na^+ etc. – small alkali ions. The injected electrons are trapped by some W^{6+}, forming W^{5+} sites. The coloration is attributed to the inter-valence charge transfer transition between W^{6+} and the newly formed W^{5+} [3]. The intercalated compound $MxWO_3$ is known as tungsten bronze.

It is known that the electrochromic response in WO_3 is superior to many other electrochromic materials, because it shows a stronger and more uniform absorption of light in the coloured state.

2. Experimental

The film deposition was carried out using an A-400VL vacuum installation. Reactive sputtering of a tungsten target (purity 99.99%) in the presence of oxygen, as the reactive gas, was used. The main parameters of the RF reactive sputtering were precisely tuned to get films with optimum properties. The thickness was controlled by the RF power (cathode voltage) and the deposition time. The oxide structure was controlled by the oxygen partial pressure. To obtain stoichiometric WO_3 films, values of the oxygen partial pressures of more than 1.10^{-4} Pa were used. The films were deposited on unheated substrates.

The structures were modified by consequent thermal treatment at temperatures of 250-300 ºC.

WO_3 films of various thickness (300 nm – 800 nm) were deposited by RF reactive sputtering on conductive glass. The substrates were cleaned with detergent and flushed with de-ionized water. Finally, the substrates were sequentially rinsed with acetone, ethanol and isopropyl alcohol and dried in a high-purity nitrogen gas stream. Processing and microstructure play a key role in determining the electrochromic properties of the WO_3 thin films. In order to be more electrochromic, the film structure should be porous. It has been reported that the optical absorption of WO_3 films upon H^+ or Li^+ ion insertion is influenced by the crystallinity, microstructure and composition of the film [4,5]. As-deposited WO_3 films are predominantly amorphous. After heat treatment at temperatures higher than 250ºC, the WO_3 crystallizes. The as-deposited amorphous WO_3 films were subjected to various annealing temperatures to obtain films containing various degrees of the amorphous or crystalline phases. The films were annealed at progressively increasing temperatures ranging from 250 ºC to 500 ºC, in air environments.

The structural properties of the films were characterized using Raman spectroscopy. This showed that amorphous WO_3 films remain as an amorphous phase at low temperatures, begin to crystallize at 250 ºC and are much more crystallized at 500 ºC. The Raman study was performed with a SPEX 1403 Raman double spectrometer, equipped with a photomultiplier, working in photon counting mode. The 488 nm line of an Ar^+ ion laser was used for excitation. The laser power on the samples was 50 mW, in the spectral range 100 - 1200 cm^{-1}. The measurements were taken with a 2 cm^{-1} step per point. The time was 5 s (for a pure substrate of Si - 2 s) and the spectral slit width was 4 cm^{-1}.

The optical properties of the films were investigated using UV-VIS spectrophotometry and multiangle four zone null ellipsometry. The ellipsometry wavelength was 632.8 nm. A variable angle four zone null ellipsometry method with angles of 60, 65, 70 and 75 degrees was used. UV-VIS spectrophotometry was applied, employing a Specord spectrophotometer.

Cyclic voltammetric experiments were performed in a standard three-electrode arrangement. The cell had Pt as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The electrodes were immersed in an electrolyte of 1 mol/l $LiClO_4$ dissolved in propylene carbonate (PC). The color change was automatically detected by the optical system, supplied to the cyclic voltammetry equipment via a chopped light source and a lock-in amplifier. The current density vs. voltage voltammograms were registered between -1 V and +1 V, at a scanning rate of 5 mV/s.

3. Results and discussion

3.1. Raman study of WO_3 thin films

The main region, where the characteristic Raman lines for transition metal oxides appear, is between 100 – 1200 cm^{-1}. The lower wavenumbers beneath 400 cm^{-1} are assigned to the deformation bands. The stretching vibrations occur in the region 1050 – 400 cm^{-1}.

Fig. 1 presents the measured Raman spectra of as-deposited WO_3 thin films obtained at different oxygen partial pressures. The spectrum of the silicon substrate is also given in Fig. 2, for comparison. Fig. 3 shows the Raman spectra of sputtered WO_3 thin films, annealed at different temperatures. The thickness of these films is 620 nm. The results of the Raman spectra investigations are summarized in Table 1.

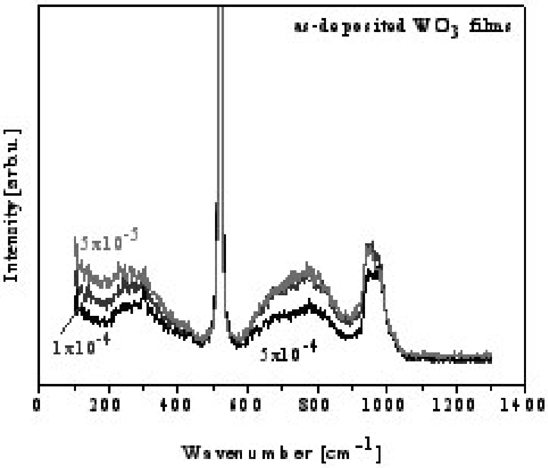

Fig. 1. Raman spectra of WO_3 thin films deposited at different oxygen partial pressures.

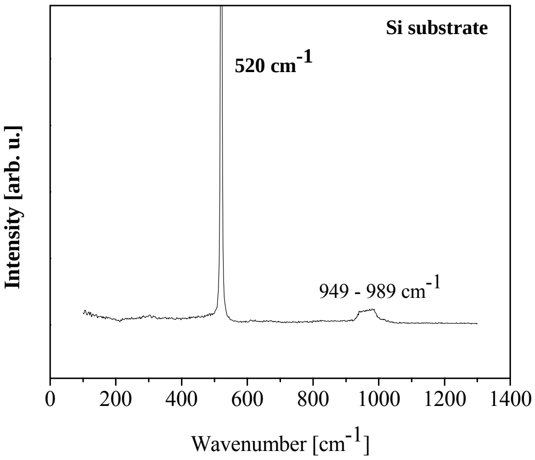

Fig. 2. Raman spectrum of a bare silicon substrate.

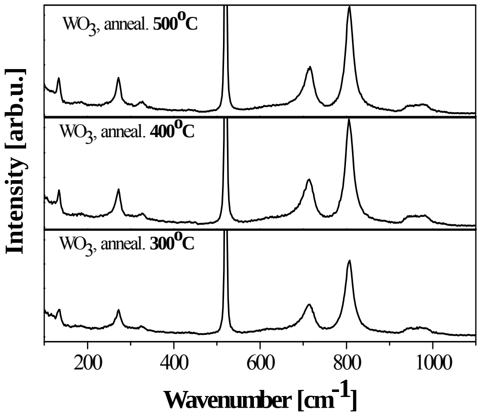

Fig. 3. Raman spectra of WO_3 thin films, annealed at different temperatures.

Table 1. Raman spectra results.

Sample	Raman band	Description
As-deposited WO_3, 1×10^{-4}	Very broad bands, located at the same wavenumbers for all samples. 226-295 cm^{-1} (centered at 267 cm^{-1}) 679- 828 cm^{-1} (centered at 766 cm^{-1}) 952 cm^{-1} – Si substrate	**Amorphous films**
As-deposited WO_3, 5×10^{-4}		
As-deposited WO_3, 5×10^{-5}		
WO_3, 1×10^{-4}, ann. 300 °C	129.5; 267.7; 326.8 (weak); 613.8 (sh) 710.3 (strong); 807.4 (very strong) 939-980 - Si	**Crystallized films**
WO_3, 1×10^{-4}, ann. 400 °C	133.2; 270; 326.8 (weak); 613.8 (sh) 710.3 (strong); 807.4 (very strong)	The Raman lines are sharper than those in the spectrum of the 300°C annealed film.
WO_3, 1×10^{-4}, ann. 500 °C	129.5; 267.7; 326.8 (weak); 613.8 (sh) 710.3 (strong); 807.4 (very strong)	The Raman lines have almost the same shape and form as those for the 400 °C annealed film.

3.2. Optical properties study of the WO_3 thin films

The study showed that WO_3, RF-sputtered on a conductive glass substrate, exhibits, even in the as-deposited state, a high optical transmittance of over 70 %. This would define a good initial transparency of the windows if eventual application as the working electrode in an electrochromic device is envisaged. Also, if WO_3 films could be fabricated by RF sputtering in a one-step process (without an annealing stage) this would be energy and time saving, and the overall technology would be cost-effective. Ellipsometric analysis showed that the refractive indices of these WO_3 thin films varied between 2.06 and 2.26. The refractive index of an as-deposited film, obtained at 1×10^{-4} Torr with a thickness of 617 nm, was n = 2.06. After annealing at 400 °C, an increase in the refractive index was obtained, n = 2.26.

3.3. Electrochromic experiments

The films showed reversible coloration upon Li intercalation. Depending on the oxygen pressure, the spectral dependences were different. It must be pointed out that these films exhibit superior electrochromic characteristics and good stability. The highest CE values, reaching 200 cm^2/C in the near IR region (700 – 800 nm) were obtained at an oxygen pressure of 5×10^{-5} Torr. In the visible range, the estimated color efficiencies were lower.

Although not fully investigated, our initial experiments with sputtered WO_3 films showed promising results with respect to applications as electrochromic materials.

The electrochromic characteristics of the sputtered WO_3 thin films, deposited at different oxygen pressures, are shown in the figures below. Fig. 4 shows the color efficiency and Fig. 5 the optical modulation of these films.

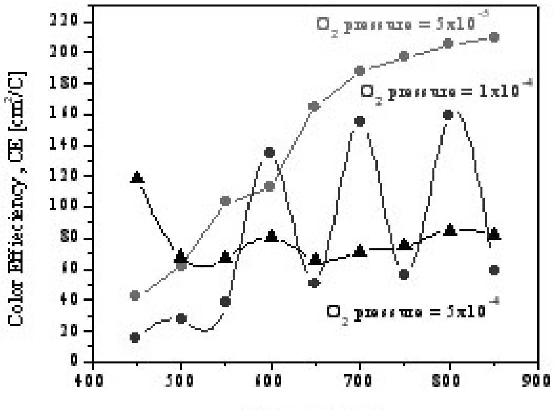

Fig. 4. Color efficiency characteristics of sputtered WO_3 thin films, obtained at different oxygen pressures.

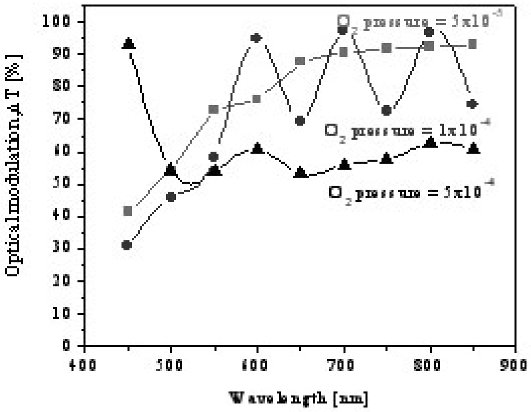

Fig. 5. Electrochromic optical modulation characteristics of sputtered WO$_3$ thin films, obtained at different oxygen pressures.

4. Conclusions

The reactive sputtering method was found to be suitable for the deposition of transparent thin films of WO$_3$. The process applied does not require heating of the substrate. All the films were highly transparent when deposited on conductive glass. Although not fully investigated, our initial experiments with sputtered WO$_3$ films show superior optical performance, a colour efficiency reaching 200 cm^2/C and an optical modulation exceeding 90 %.

Acknowledgements

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