



Highly porous tungsten oxides for electrochromic applications

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ABSTRACT

The electrochromic (EC) properties of porous and highly porous tungsten oxide films deposited by heating a metallic wire in rough vacuum, without and with the injection of oxygen pulses on the filament, respectively, were investigated by proton intercalation using conventional and polymeric electrolytes. It was found that the EC properties like coloration efficiency and cyclic durability of coloration–bleaching process of the hot wire deposited tungsten oxide (HW-WO₃) films strongly depend on the deposition environment and growth parameters. The highly porous films are initially very transparent (more transparent than fused silica, for example) and exhibit high coloration efficiency due to easier intercalation of the proton within their structure. These results suggest that the highly porous films obtained with the hot wire method combined with rapid injection of O₂ exhibit superior EC performances than denser films deposited by conventional deposition methods.

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1. Introduction

Electrochromism is the reversible change of color exhibited by various materials induced by the application of an electrical current or a potential difference [1–3]. Electrochromic (EC) materials have been studied on a fundamental physio-chemical basis for many years, with practical applications as recent development. Many different classes of materials display EC characteristics. Inorganic EC materials are mainly transition metal oxides (TMOs), such as tungsten, cobalt, manganese, nickel, palladium, cerium, rhodium, iridium, ruthenium, titanium and molybdenum oxides [4–10]. Among them, tungsten oxide (WO₃) is one of the most widely studied [11–22]. The electrochromism in WO₃ films may be observed in EC devices composed by the film sandwiched between a transparent electrode and an electrolyte and a counter electrode. Application of a negative voltage between the transparent and the counter electrodes causes a blue coloration of the initially transparent WO₃ film while inversion of the biasing voltage renders this film transparent again (bleaches the film). The coloration may be divided in two parts: an initial fast followed by a second slower one. The former has been attributed [23] to the injection of electrons into the initially empty conduction band of the WO₃, the bottom of which is formed by the overlap of the d bands of the metallic ions. Due to the low mobility of d electrons and their localization near the metallic ions, they correlate; the

electrostatic repulsions between them causing the splitting of this d-like band in two sub-bands. The electronic transitions between these two bands cause the initial fast part of the observed coloration. During this initial period the electrical neutrality of the whole EC device is insured by the formation of a space charge zone at the interface WO₃/electrolyte. In parallel to the injection of electrons also ions diffuse from the electrolyte into the WO₃, which is a process much slower than the former accentuating further the coloration. Upon bias reversal the bleaching process may also be divided in an initial fast part related to the extraction of electrons and a slower one related to the rejection of ions back into the electrolyte.

In order to achieve better EC performances, these two processes should be facilitated and promoted with the aims of achieving higher optical contrast and faster reaction kinetics. However, the ion diffusion in and from the ECOs thin films is generally the limiting step. Tailoring the inorganic EC material into various types of nanostructure is a promising route, which promotes both types of processes and hence achieving better EC performance mainly because large surface to volume ratios can be achieved. The advantages of employing WO₃ nanostructures as working electrode have been recently demonstrated by comparison to the EC performances of thin films [5,21].

In our previous study we examined the EC properties of WO₃ thin films deposited with the chemical vapor deposition technique, by using a polymeric electrolyte [20]. In the present work we examine the EC performances such as coloration efficiency and time stability of highly porous WO₃ films obtained by a novel

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technique based on the so-called hot wire vapor deposition. The method of hot wire vapor deposition proceeds via the sublimation of the native oxide of the wire, therefore it is limited for very thin films only. In order to overcome this difficulty, small amounts of O₂ (termed as O₂ “pulses”) were injected into the reactor during deposition using atomic layer deposition (ALD) valves, so the wire is superficially oxidized again and the deposition continues. With this method highly porous WO₃ were obtained exhibiting superior EC performances as reported in this work.

2. Experimental

The deposition system used to prepare large area, porous tungsten oxide films is similar to the one previously reported [24]. The main difference is the use of a PC-driven needle valve allowing for the flow of various gases such as O₂, N₂ through the reactor. The same PC also drives the atomic layer deposition (ALD) and the various shut-off valves. The ALD valves and the associated gas lines (containing valves and tubing) are heated, allowing for the injection of a variety of precursors into the reactor. The system is actually a hot-wire ALD system but in this work the filament played the role of the precursor while the deposition ambient was set by a gas flow (of O₂, N₂) and O₂ was injected through an ALD valve.

Depositions were carried out on indium tin oxide (ITO) substrates with a sheet resistance of 15 ohm per square, which were used as the bottom electrode. After WO₃ film deposition the polymeric electrolyte, consisting of a polymethyl methacrylate (PMMA) 4% w/w solution containing also the 12-phosphotungstic acid hydrate (POM) in a concentration 1:1 of the polymer mass, was applied by using the dip coating technique [20]. The device was finished with the insertion of the ITO top electrode.

The deposited WO₃ films were characterized with a variety of techniques including spectroscopic ellipsometry within the 350–1000 nm range using a J.A Woolam Inc. M2000F rotating compensator ellipsometer (RCE™) running the WVASE32 software at an angle of incidence of 75.14°. It is well known that spectroscopic ellipsometry measurements, analyzed with the aid of the effective medium theory, are able to yield the void content of films and their thickness. This method has been applied in the past to obtain the porosity of hot-wire deposited WO₃ films [24]. A LEO Supra 35 VP was used for the SEM measurements. FTIR spectroscopy measurements (in absorption mode) were made using a Bruker spectrometer, while transmittance measurements of the EC devices were performed with a Perkin-Elmer Lambda 40 Spectrometer.

3. Results and discussion

The influence of the deposition environment and growth parameters on the deposition of hot wire tungsten oxide films used as the active components in EC devices was initially studied with FT-IR spectroscopy (Fig. 1). Two types of nearly stoichiometric tungsten oxide films can be obtained. Films deposited in pure oxygen by heating the W filaments are termed as HW-WO₃, while those deposited in N₂ environments through the rapid injection of O₂ “pulses” within the hot W filament, are termed as HWALD-WO₃, both shown in Fig. 1. As shown in this figure, both films are exhibiting the $\nu(\text{O}-\text{W}-\text{O})$ and $\nu(\text{W}=\text{O})$ bands in wavenumbers corresponding to fully oxidized tungsten trioxide (in 665 and 966 cm⁻¹ the HW-WO₃ and in 674 and 969 cm⁻¹ the HWALD-WO₃, respectively) indicating that both are nearly stoichiometric [25,26]. Also, small shifts of both $\delta(\text{OH})$ and $\nu(\text{OH})$ bands, due to structurally bound water molecules, to lower wavenumbers indicate possibly that water molecules may participate in that slight reducing process.

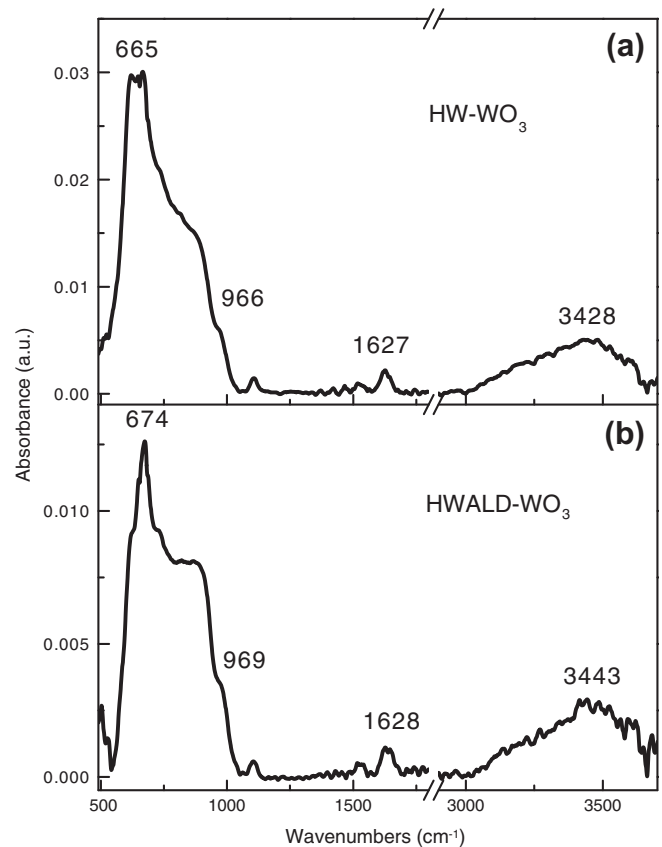


Fig. 1. FTIR spectra of a (a) HW-WO₃ and (b) HWALD-WO₃ tungsten oxide films with a thickness of 100 nm, deposited in O₂ environment and in N₂ environment with the injection of 5 O₂ pulses, respectively.

In Fig. 2, the dispersion of the real (Fig. 2a) and imaginary (Fig. 2b) part of refractive index of 100 nm HW-WO₃ and HWALD-WO₃ films is reported. For comparison, the corresponding dispersions for a chemically vapor deposited (CVD) WO₃ film are also shown. It is observed that the *n* and *k* curves of HWALD-WO₃ films show similar variation with those of the HW-WO₃ but smaller values, which is a strong indication for higher porosity and implies a high transparency (especially the HWALD WO₃ film, whose refractive index is smaller than 1.45, is more transparent than fused silica). Both films have their refractive indices much smaller than the corresponding ones of the CVD-WO₃ in the whole wavelength spectrum.

In Fig. 2(c) the evolution of the porosity with the thickness of both hot wire deposited tungsten oxides is depicted. It can be clearly seen that both films are highly porous. Especially, the HWALD-WO₃ film, formulated with the injection of one O₂ pulse for each 5 s after having turned on the filament, exhibits 60% porosity for the thickness of 100 nm used in this study, while the corresponding porosity of the HW-WO₃ film with the same thickness, deposited in O₂ environment, is about 40%. From this Figure it is evident that highly porous, stoichiometric tungsten oxide films in large areas can be formulated, by using the hot wire ALD technique. Regarding the growth mechanism of porous HW-WO₃ films one can speculate a random deposition of WO₃ species emitted by the filament and condensed subsequently on the substrate, on which the surface diffusion is limited due to its low temperature. Similar considerations may be done for HWALD films but now the WO₃ species produced on the filament are more disordered due to their rapid formation (ALD valves turn on and off within 50 ms).

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