

Electrochromic Devices Based On Electrodeposited WO₃ Films With Modified Surface Morphology.

G. Leftheriotis^{1*} and P. Yianoulis¹

¹ Energy and Environment Lab, Physics Department, University of Patras, Rion, 29500, Greece

*glefther@physics.upatras.gr

Tungsten oxide is a well known material with electrochromic properties, suitable for application in switchable electrochromic glazing for solar control in buildings, large area displays and gas sensors [1]. It can be deposited in the form of a thin film with use of various methods, such as vacuum techniques (thermal evaporation, electron beam gun deposition and sputtering) and with chemical methods (sol-gel deposition, spin coating, spray pyrolysis and electrodeposition) [1, 2]. Of these, electrodeposition is a straightforward technique that does not involve the application of complicated and expensive instrumentation (required in the case of vacuum methods) and that can be readily upgraded to coat large areas at high throughput. Furthermore, it permits the exact control of the film thickness and is suitable for the fabrication of composite films that incorporate two (or more) compounds, such as WO₃ – CeO₂, WO₃ – TiO₂, etc [3].

The surface morphology and microstructure of WO₃ films determines their electrochromic performance. Films that possess an 'open' structure, caused by high porosity or by extensive grain boundaries, are more suitable to function as electrochromics since their form facilitates the intercalation of metal ions responsible for coloration [4, 5]. Different methods yield films with different morphologies and structure. With electrodeposited films, a variety of morphologies and microstructures can be obtained by variation of the starting materials, the solution chemistry [6], by alterations in the applied voltage or current [7] and by post deposition thermal treatment [8].

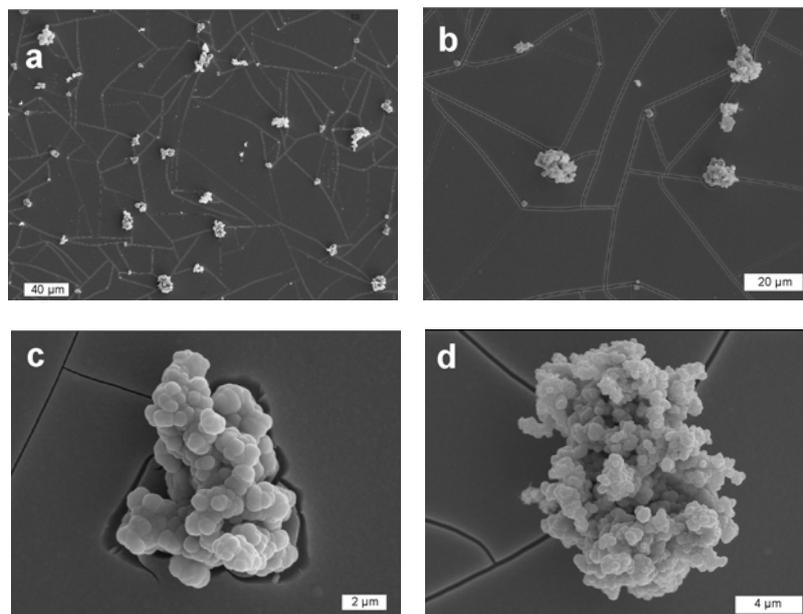


Fig. 1. Scanning Electron Microscopy (SEM) photographs of a WO₃ film electrodeposited 48 hours after the precursor formation

In the present study, we propose a very simple method for the alteration of the surface morphology of electrodeposited WO₃ films. Evidence is presented that the peroxotungstic acid precursor (synthesized in a similar way to that presented in [9]), tends to conglomerate within its solution. If enough time is allowed before film deposition (typically 48 hours), large conglomerates are formed, that possess a grape-like structure. During electrodeposition, these arrive on the substrate surface and are incorporated into the resulting WO₃ film that is being developed, as shown in Fig 1. This phenomenon can be used advantageously in order to modify the resulting WO₃ film morphology: Films with such conglomerates incorporated into their structure have a high effective surface area, improved ion mobility and enhanced electrochromic properties.

The above principle has been applied for the electrodeposition of WO_3 films 48 hours after the precursor formation. They exhibit modified morphology (as shown in Fig.1), with typical thickness of **1.300 nm** and Li ion diffusion coefficient as high as **$4.5 \times 10^{-10} \text{ cm}^2/\text{s}$** , which is more than an order of magnitude larger than that of typical evaporated tungsten oxide films [1, 10]. These films exhibit promising electrochromic coloration properties: In Fig. 2, cyclic voltammetry (CV) plots of two WO_3 films appear, one deposited immediately after the solution synthesis and another deposited 48 hours later. It becomes evident from a comparison of the two plots that the latter film performs best, as it exhibits a larger negative (coloration) current (up to $-1.3 \text{ mA}/\text{cm}^2$). Furthermore, the area of the cyclic voltammogram which is a measure of the charge intercalated into the film [10, 11], is larger for the latter film.

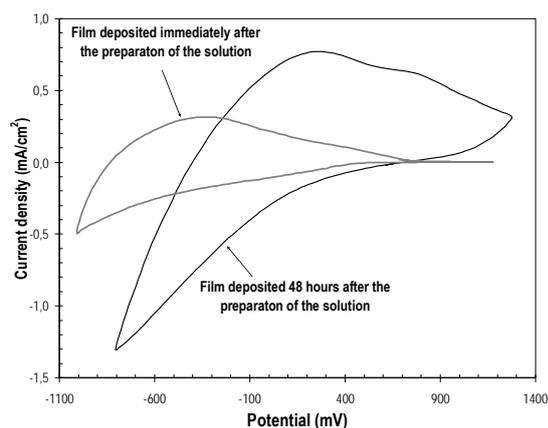


Fig.2: CV plots of electrodeposited WO_3 films

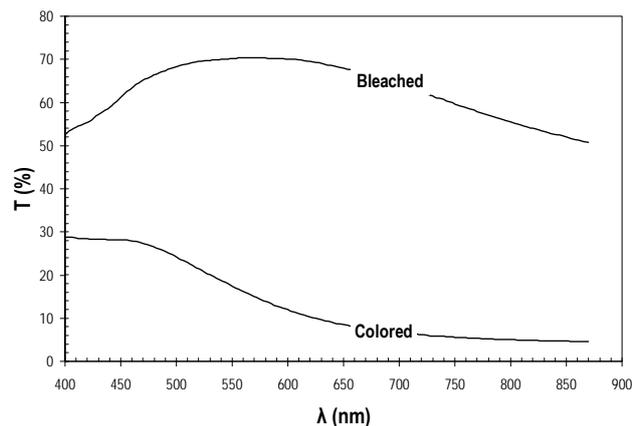


Fig. 3: Transmittance (T) spectra for the coloration of an EC device with an electrodeposited WO_3 film

Electrochromic (EC) devices incorporating the electrodeposited WO_3 films of the form K-glass/ WO_3 /1M LiClO_4 -PC (liquid electrolyte)/K-glass were fabricated in the following manner: Two K-glass sheets (a plain one and one with the tungsten oxide film) were arranged facing each-other, slightly displaced along their longitudinal axis in order to reserve space for the formation of electrical contacts. A cavity was formed between the two glass sheets with use of silicone. The cavity was filled with the liquid electrolyte and sealed with silicone. Electrical receptacles were created on both glass sheets with use of copper adhesive tape. As can be seen in Fig. 3, the increased surface roughness of the WO_3 films does not impede the optical properties of the device. Indeed, in the bleached state the device appears significantly transparent ($T=70\%$ at 550 nm). As it becomes progressively colored, ($T=17\%$ at 550 nm) a satisfactory contrast ratio is achieved. The fabricated devices are stable and can withstand several hundreds of coloration- bleaching cycles with no evident degradation of their performance.

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