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Development of electrodeposited WO_3 films with modified surface morphology and improved electrochromic properties

G. Leftheriotis [*], P. Yianoulis

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

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ABSTRACT

A simple method for the morphology modification of electrodeposited WO_3 films is presented. It is based on the tendency of the peroxotungstic acid precursor to conglomerate within its solution towards grape-like structures. It has been shown that WO_3 films deposited 48 h past the precursor formation incorporate the aforementioned formations in their structure and have a higher effective surface area and improved ion mobility compared to similar films prepared immediately after the synthesis of the precursor. We have used the above method to fabricate electrodeposited WO_3 films with modified morphology, 1300 nm thick, with Li ion diffusion coefficient values as high as 4.5×10^{-10} cm^2/s. These films exhibit promising electrochromic coloration properties.

1. Introduction

Tungsten oxide is a well known material with electrochromic properties. 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) [1,2–4]. 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 (unlike spin-coating) and is suitable for the fabrication of composite films that incorporate two (or more) compounds, such as WO_3–CeO_2, WO_3–TiO_2, etc [5,6,7].

The surface morphology and microstructure of WO_3 films determine 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 [8,9]. Different methods yield films with different morphologies and structure. It is well known [1] that sputtered WO_3 films tend to be polycrystalline while thermally evaporated and e-gun deposited ones are amorphous [10]. Sol–gel derived films are known to be amorphous or polycrystalline with grains of various sizes, according to solution chemistry and post-deposition treatment [11,12]. The morphology of spray pyrolysis WO_3 films strongly depends on the substrate temperature during their fabrication [2,4]. As for electrodeposited films, a variety of morphologies and microstructures can be obtained by variation of the starting materials and the solution chemistry [8,9,13,14], by alterations in the applied voltage and current [13], by post-deposition thermal treatment [15], and by other techniques.

In the present paper, we propose a very simple method for the alteration of the surface morphology of electrodeposited WO_3 films. Evidence is presented that the peroxotungstic acid precursor (synthesized in a similar way to that presented in [16]), tends to conglomerate within its solution. If enough time is allowed before film deposition, large conglomerates are formed, that possess a grape-like structure. During electrodeposition, these arrive on the substrate surface and are incorporated into the resulting WO_3 film that is being developed. The films thus formed have enhanced ion mobility, possibly due to their grain size, their higher effective surface area and the extensive cracks that appear through them.

2. Experimental

2.1. Preparation of the peroxotungstic acid solution

For the preparation of the peroxotungstic acid solution 6.5 g of W powder (99.9 pure) was dissolved in 40 ml H_2O_2 (30% dense) and 4 ml of distilled water. The addition of W powder into H_2O_2 was conducted in a chilled water bath under continuous agitation. Caution must be taken during this process: the solution temperature should not exceed 5 °C, as the peroxotungstic acid formation is a strongly exothermic reaction. Then, the tungsten-peroxide solution was kept in a refrigerator at about 2 °C. At such low temperatures it takes about 7 days for all of the W quantity to be dissolved. At that stage, a clear solution of a slightly yellowish color is obtained. However, this solution still

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[*] Corresponding author. Tel.: +30 2910 997 449; fax: +30 2910 447 472.
E-mail address: glefther@physics.upatras.gr (G. Leftheriotis).

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contains an excess quantity of H_2O_2 and in order to dispose of it, a further 5 days at low temperature (2 °C) is required. The gradual reduction of peroxide at low temperatures was preferred over other less time consuming methods (such as treatment with tungsten bronze) as it prevents the precipitation of WO_3 sediment (yellow powder). The peroxotungstic acid colloidal solution [19], obtained by this procedure can be kept at 2 °C for a few weeks.

2.2. Electrodeposition of WO_3

Part of the above solution was mixed with an equal volume of anhydrous ethanol at room temperature under continuous agitation and yielded a bright yellow liquid, which was pre-heated to 60° for 15 to 20 min.

The electrodeposition of WO_3 from this solution was performed under a voltage of −450 mV for 10 min, with current densities in the order of 1–2 mA/cm^2. A typical three-electrode configuration was used with a SnO_2:F coated glass sheet (trade name: K-glass) with dimensions 2.5 cm × 3.5 cm as the working electrode, an Ag/AgCl reference electrode and a Pt counter electrode.

The films obtain a deep blue color during the preparation process, which vanishes almost immediately after their removal from the solution. Rinsing with de-ionised water and drying in air follows.

This process yields WO_3 films of good quality with a typical thickness of about 1500 nm, and with good adherence to the substrate. Films of different thickness can be prepared by varying the duration of the electrochemical deposition process.

The aforementioned solution can be used for several electrodepositions for about a week. However, the morphology and properties of films deposited immediately after the solution preparation are significantly different than those of films deposited from the same solution two or more days later. The main difference is the formation of conglomerations within the solution that increase in magnitude with time. During electrodeposition these conglomerations “bombard” the developing film surface, create cracks and alter the film electrochemical properties. This effect will be discussed in detail in the following sections and is the central subject of this paper. One week post-preparation, the solution becomes dysfunctional, giving films of poor properties. Several weeks later, a thick gel of yellowish color precipitates with a mixture of ethanol and water above it.

2.3. Instrumentation and experimental techniques

The thickness of the films was measured by an Ambios XP-1 profilometer. This instrument was also used in order to assess the surface morphology of the films.

Scanning electron microscopy (SEM) pictures of the films were taken using a JEOL 6300 microscope. This instrument has capabilities of composition analysis of the films with use of the Energy-Dispersive X-ray Spectroscopy (EDS) method.

In order to assess the electrochemical properties of the films, cyclic voltammetry tests and experiments using the Galvanostatic Intermittent Titration Technique (GITT) were performed using the following instruments: a potensiostat–galvanostat (AMEL, model 2053), a function generator (AMEL, model 586) and noise reducer (AMEL NR 2000). The electrochemical cell used for these experiments has already been described elsewhere [10]. During the cyclic voltammetry tests, the potential between the working (WO_3/K-glass) and the reference (Pt) electrode was varied linearly in the range (−1.1 V, +1.3 V) at a rate of 50 mV/s. During the GITT experiments, a series of 100 square current pulses with amplitude 0.2 mA and duration 5 s was fed into the electrochemical cell, each followed by an equilibration period of 30 s. The potential between working and reference electrodes (corresponding to the emf of the film) versus the inserted charge density has been measured. The “intercalation parameter” x in the resulting Li_xWO_3 films and the Li ion diffusion coefficient has been calculated as described in our previous work [17]. In both experiments, a computer has been used to store and manipulate the data.

Electrochromic (EC) devices incorporating the electrodeposited WO_3 films of the form K-glass/WO_3/1 M $LiClO_4$-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.

The transmittance (T) and reflectance (R) spectra (at normal incidence) of the EC devices during different coloration stages were recorded with use of a Perkin Elmer Lambda 650 UV/VIS Spectrometer.

3. Results and discussion

3.1. Surface morphology of the films

In Fig. 1, a SEM picture appears of a WO_3 film deposited immediately after the preparation of the precursor solution. The film appears to have irregularities (bumps) spherical in shape, of 100–500 nm in diameter. A completely different picture can be seen in Fig. 2, in which SEM photographs of a WO_3 film deposited 48 h after the solution preparation appear. As can be seen in Fig. 2a and b, the film surface is littered with “chunks” of irregular shape, with dimensions up to 10–20 μm. These “chunks” have a grape-like structure (as shown in Fig. 2c and d) and comprise of particles nearly spherical in shape, and 100–500 nm in diameter. In between these “chunks”, the film surface appears smooth and homogeneous. Furthermore, cracks are present throughout the film surface, that start or end at the positions of the “chunks”. The composition of the films of both Figs. 1 and 2 was examined using the JEOL 6300 microscope with the EDS method. In all cases, peak characteristics of WO_3 were found. The same applies for the “chunks”. Therefore there is no doubt that all the features observed belong to tungsten oxide formations.

The surface profile of these films was investigated by a step profilometer and the results appear in Fig. 3. It can be confirmed once more that the films deposited 48 h after the solution formation have considerably larger surface roughness, compared with films deposited immediately after the solution preparation. Both films appear to be 1000–2000 nm thick. The large “chunks” shown in Fig. 2 adhere well to the underlying film: The surface profiles were measured again after electrochemical testing and no change was observed.

A possible explanation of these findings follows: the spherical bumps (100–500 nm in diameter) are present in the precursor solution during its synthesis. During the deposition that takes place

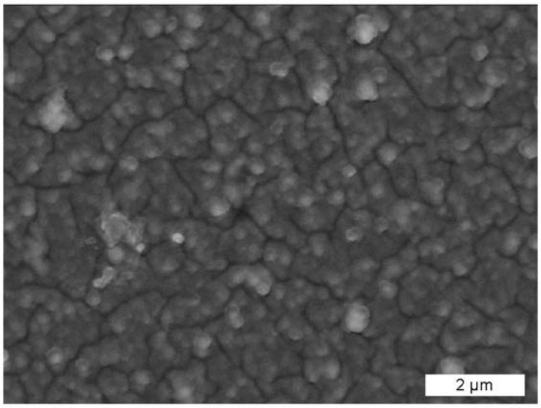

Fig. 1. SEM photograph of a WO_3 film electrodeposited immediately after the precursor formation.