



Optimization of mixed conductivity through nanostructure control in WO₃ thin films



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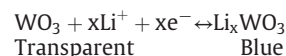
ABSTRACT

Tungsten trioxide (WO₃) thin films have become increasingly important in recent years both from the fundamental research point of view as well as for their application potential as smart windows for energy efficiency. The electrochromic coloration efficiency as well as the kinetics of coloration are very important for these applications. Although much emphasis is placed on rendering the films optically efficient by working with nanostructured WO₃ films, not much work is done to optimize their electrical properties, especially their mixed conductivity (ionic and electronic) which is equally important. In this work, we have attempted to optimize the mixed conductivity of the thermally evaporated WO₃ thin films by systematically varying their nanostructure. Based on our previous work, working pressure (between 1.3×10^{-3} and 0.13 Pa) has been used as the control parameter to induce varying nanostructure in the films. The grain size and the film roughness are found to increase systematically with the working pressure. The electronic and ionic conductivities have been deduced from the electrochemical measurements. With increasing working pressure in the chamber the ionic conductivity is found to increase systematically while the electronic conductivity decreased. The lithium ion diffusion is also found to increase with increasing working pressure. The optimum values are found to be around a working pressure of 7.3×10^{-2} Pa, yielding values of around 5.5×10^{-7} ($\Omega^{-1}\text{cm}^{-1}$) and 5.5×10^{-10} ($\Omega^{-1}\text{cm}^{-1}$) for ionic and electronic conductivities, respectively.

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1. Introduction

Electrochromic (EC) materials whose optical properties can be reversibly changed in the visible and infrared spectral region through the application of a small electric field have become increasingly important from their application point of view in various interactive devices. Amongst the transition metal oxides (TMO), Tungsten trioxide (WO₃) exhibits the most efficient coloration making it the most sought after material for applications such as smart windows, display devices and more. The reversible coloration in these thin films occurs via the double injection of ions, such as lithium, and electrons as shown below.



Both amorphous and polycrystalline WO₃ films exhibit EC coloration under this double injection, although the coloration phenomenon is distinctly different in the two types of films. In amorphous films the

coloration is expected to occur via the trapping of the injected electrons on the W⁺⁶ tungsten sites and their transfer to W⁺⁵ sites. The blue coloration ensues through the intervalence transfer of the trapped electrons between the W sites through the absorption of incident light [1]. Hence, amorphous WO₃ films exhibit a more pronounced coloration in the visible region of the spectrum. The EC coloration in polycrystalline film, on the other hand, originates from reflectance modulation arising from the inserted electrons behaving as free electrons. The EC coloration is found to depend very strongly on the film nanostructure which in turn is found to depend on the various deposition parameters including the heat treatment during and after the film deposition. Thus nanostructure control has become an important aspect in recent years in tailoring the electrochromic behavior of the WO₃ films [2]. As can be seen from the above reversible reaction and the double insertion required to bring about the EC coloration, both the aspects of optical and electrical properties are very important. The double insertion dictates that the electrical conductivity of both the species inserted (ions and electrons) be optimized in order to improve EC kinetics and coloration. Based on the prospect of increased internal surface area leading to efficient EC coloration, more and more research work is being focussed on nanostructured thin films with high porosity [3]. This nanostructure induced in WO₃ film using various techniques may seem to enhance the coloration efficiency but is prone to inducing impediments in the overall EC

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kinetics when the optical and electrical properties are considered simultaneously. Increasing grain size in nanostructured films may be conducive to ionic conductivity, but may end up decreasing the electronic conductivity due to the increased grain boundary scattering. Dense or coarse grained films on the other hand have better electronic conductivity, but may limit the ionic conductivity and the internal surface available for the charge transport. Since an efficient double insertion and extraction is primordial for a stable and effective EC operation of the WO₃ thin films, it is essential to optimize the ionic and electronic conductivities of the films. The aspects related to the EC kinetics become crucial, especially when the films are integrated in a device form. Although, an enormous amount of research work has been carried out on EC coloration of nanostructured WO₃ films, very little attention is paid to simultaneously optimizing the optical and electrical behavior [4]. Even in the case where the optical and electrochemical kinetic studies are carried out in detail, the simultaneous measurement of ionic and electronic conductivity is very sporadic [5].

In this work, we have examined the correlation between nanostructure and the electrical properties in amorphous WO₃ films. We have carried out a systematic variation of the nanostructure of WO₃ thin film in order to simultaneously optimize the mixed (ion and electron) conductivity. Based on our earlier work [6], we have used the working pressure in the deposition chamber as the control parameter in the present work. The high pressure in the chamber is expected to cause the scattering of the evaporated particles and to their in-flight growth before condensing on the substrate to form the thin film. This method has been found to be an efficient approach for the nanostructure control. To the best of our knowledge such a work regarding the simultaneous measurement and optimization of conductivities through nanostructure control has not been carried out. This aspect seems to be an important one in the design and efficient operation of the EC devices based on WO₃ films.

2. Experimental details

WO₃ thin films were prepared by the thermal evaporation technique. The target-substrate distance was fixed at 20 cm. ITO coated glass substrates cooled down to 278 K using a Peltier device, were used in this work in order to render the high pressure sublimation and condensation on the substrates efficient. A small area of the substrate coated with ITO was masked in order to have access to the ITO for the electrical measurements. The source material was high purity (99.9%) WO₃ powder obtained from Alfa Aesar held on a heated tungsten filament. The chamber was evacuated to an initial high vacuum of 1.3×10^{-4} Pa before a controlled introducing of high purity Argon gas into the chamber to different working pressures. WO₃ samples were deposited at the working pressures of: 1.3×10^{-3} , 6.6×10^{-3} , 1.3×10^{-2} , 6.6×10^{-2} , 8×10^{-2} , and 1.3×10^{-1} Pa. All the deposited films were estimated to have a thickness of 200 nm using a quartz crystal monitor placed near the substrate. The deposition rate was 7.2 nm/min.

After the deposition, each of the samples was annealed at a temperature of 523 K for 1 h in air to render the films nearly stoichiometric and stable against humidity. The surface morphology of the thin films was studied by Atomic force microscopy (AFM) using Dimension 3100 series of Digital Instruments with VT102 vibration isolation table. The electronic and ionic conductivities of all the samples were measured by impedance spectroscopy using BioLogic Science Instrument (VSP300 VMP3) in the frequency range from 100 Hz to 1 MHz of a potentiostatic sine wave signal of different amplitudes. To do such a measurement, an adhesive conducting copper strip was attached on the edge where ITO was exposed. The sample was then immersed in 1 M solution of lithium perchlorate (LiClO₄) dissolved in propylene carbonate (PC) used as the electrolyte for the electrochemical measurements. A traditional three electrode type electrochemical cell was used for lithium intercalation study and. The WO₃ thin film deposited on ITO coated glass as described above was used as the working electrode (WE). A carbon rod and a

standard calomel electrode (SCE) were used, respectively, as counter electrode (CE) and reference electrode (RE). The voltage was applied between the WE and the RE and the current was measure between the WE and CE.

3. Results and discussion

3.1. Surface morphology

The surface roughness and grain size were determined using the atomic force microscopy (AFM). In nanostructured films, it is important to determine the effect of working pressure on the grain size as well as the roughness of the deposited films. Fig. 1 shows the top view AFM images of the WO₃ thin films deposited at different working pressures. It is quite evident from this figure that the surface morphology is strongly dependent on the working pressure. The sample deposited with a working pressure of 1.3×10^{-3} Pa (Fig. 1a), presents a flat surface made up of tiny grains with lower roughness compared to the subsequent images (Fig. 1b to e) of films deposited with increasing pressure. With increasing pressure the granularity is seen to increase along with the film porosity. This phenomenon could help increasing the number of ions intercalated during coloration. By increasing pressure the surface structure becomes increasingly rough with both the grain size and their aggregates increasing systematically. It was not possible to measure the AFM of the sample with the highest pressure of 1.3×10^{-1} Pa studied, since its grain size was out of the measurable range of the AFM system.

The variations of grain size and average roughness with pressure as calculated from the AFM images of Fig. 1 are presented in Fig. 2. As seen in this figure, both these parameters increase with the working pressure. Johansson et al. [7] have reported a similar behavior in their polycrystalline WO₃ films deposited at substrate temperature of 553 K and annealed at 673 K. The reduction of mean free path of the evaporated particles at higher pressure is expected to cause a higher probability of coalescence of the particles and lead to the in-flight coalescence and grain growth. Thus higher pressure leads to a higher grain size and a higher film roughness. Such effects are also seen by Takahashi et al. [8]. In their study of the deposition rate in sputter deposited WO₃ with different working pressures. The grain size and related parameters of our samples are also shown in Table 1 as functions of the working pressure.

3.2. Electrochemical properties

The cyclic voltammetry (CV) was carried out by applying a linearly increasing voltage from an initial value up to peak value and returning to the initial value. The obtained response from the sample is the current variation versus applied potential. The results of the CV carried out on the WO₃ films deposited at various pressures are presented in Fig. 3. These closed loop CV cycles were obtained by varying the triangular potential between -1 V and $+1$ V and with a scan rate of 10 mV/s. A color change from transparent to dark blue and back was observed along the CV cycles due to the ensuing insertion/extraction of both ions and electrons into the WO₃ films. The maximum current in the CV cycle increased as the working pressure increased due to the change in film morphology discussed above. The increasing film porosity seems to facilitate the insertion and extraction of the intercalated species. From the CV cycles the chemical diffusion coefficient (D) for lithium ions in WO₃ thin films was calculated from the Randles-Sevcik equation [9]:

$$i_p = 268600 n^{3/2} A D^{1/2} C v^{1/2}$$

where i_p is the maximum current (A)

n the number of electrons transferred in the redox event ($n = 1$ for Li⁺)

A is the electrode area (cm²)

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