Applied Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Preparation of nanostructured tungsten trioxide thin films by high pressure sublimation and condensation

B. Abdel Samad*, J. Thibodeau, P.V. Ashrit

Thin Films and Photonics Research Group, Department of Physics & Astronomy, Université de Moncton, Moncton, NB, Canada E1A 3E9

ARTICLE INFO

Article history:
Received 31 October 2014
Received in revised form 6 March 2015
Accepted 11 March 2015
Available online xxx

Keywords:
Electrochromism
Tungsten trioxide
Thin films
Nanostructured films

ABSTRACT

Thin films of tungsten trioxide (WO_3) have gained increasing importance due to their interesting chromogenic properties and for their high application potential in electrochromic devices. It is very well known that their electrochromic switching properties depend very sensitively on their nanostructure. Hence, a vast majority of the research work carried out in this domain at present is dedicated to the various techniques of controlled inducing of a nanostructure in these WO_3 thin films in order to enhance their electrochromic performance.

In the present work we have carried out a systematic study of the nanostructured WO_3 thin films by using a novel technique of varying the source–substrate distance in a high pressure sublimation and condensation method. This technique has been found to be very efficient in controlling the grain size and thus the nanostructure of the deposited films. A correlation is established between the optical and electrochromic properties of the WO_3 films and the induced nanostructure. The electrochromic properties are studied by a dry lithiation process developed in our laboratory. The results indicate a strong dependence of the film nanostructure on the source–substrate distance which influences quite sensitively the electrochromic properties. These results are expected to help design electrochromic devices suitable for different applications.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Tungsten trioxide is one of the most interesting materials exhibiting a wide variety of chromogenic properties, i.e. reversible coloration under the influence of various external forces. Tungsten trioxide (WO_3) thin films have been investigated exhaustively for their electrochromic properties. Under the application of a small electric field and the ensuing insertion of x number of electrons (e^-) and ions (M^+), the normally transparent WO_3 thin films exhibit a reversible deep blue coloration [1] as shown below.

$$\underset{\text{Transparent}}{WO_3} + xe^- + xM^+ \leftrightarrow \underset{\text{Blue}}{M_xWO_3}$$

The investigation of WO_3 thin films deposited by various physical and chemical methods have shown that their electrochromic properties depend quite sensitively on their physical properties such as structure, surface morphology, grain size and roughness. These physical properties in turn are found to depend on the method of the film preparation and the parameters used. Hence, the optical and electrochromic properties of the WO_3 thin films can be controlled via the methodology and the parameters employed. The optical properties, for example, were studied in detail by Srinivasa et al. [2] showing that WO_3 thin films deposited by RF sputtering exhibit different optical properties for different sputtering pressures and annealed at different temperatures. A faster optical switching response and a better control of the film stoichiometry have been achieved in electrodeposited WO_3 thin films [3]. The deposited films have electrochromic response better than that observed with films prepared by other deposition methods. The WO_3 film density, the structure and the optical properties were also found to be influenced by the substrate temperature [4]. Using the GLAD (glancing angle deposition) method, Beydaghyan et al. [5] have shown that the film transmittance, the porosity and the refractive index are all strongly dependent on the deposition parameters. In another work carried out in our own laboratory using the method of high pressure sublimation and condensation, it has been found that WO_3 films with varying nanostructure can be obtained using a combination of deposition and post-deposition treatment [6]. The difference in film nanostructure is found to lead to a difference in their electrochromic behavior. In this technique of high pressure sublimation and condensation, the chamber pressure becomes an important parameter. With increasing pressure, the mean free path

* Corresponding author. Tel.: +1 5068584693.
E-mail address: bassel.abdel.samad@umoncton.ca (B. Abdel Samad).

http://dx.doi.org/10.1016/j.apsusc.2015.03.054
0169-4332/© 2015 Elsevier B.V. All rights reserved.

Please cite this article in press as: B. Abdel Samad, et al., Preparation of nanostructured tungsten trioxide thin films by high pressure sublimation and condensation, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.03.054

of the sublimated particles is reduced thus increasing the probability of inter-particle collision and growth. Hence, the size of the particles can be controlled in-flight, i.e. before they arrive at the substrate and condense. An in-depth understanding of the correlation between the nanostructure induced and the various fabrication methods and parameters used will lead us to tailor the optical and electrochromic properties of WO_3 thin films as per the application need.

In the present work, we have carried out the study of the optical and electrochromic properties of WO_3 thin films deposited by the high pressure sublimation and condensation method by varying the source–substrate distance at a constant chamber pressure. This approach is also expected to provide a better in-flight control of the nanoparticle size. A systematic control of the WO_3 film nanostructure seems to have been achieved through this method showing a wide variety of optical and electrochromic properties. Film thickness, porosity and grain size are also found to vary systematically. The suitability of these films for various electrochromic device applications has been underlined.

2. Experimental details

WO_3 films were deposited by thermal evaporation technique at a temperature of 6 °C on glass substrate. WO_3 powder of 99.9% purity obtained from Sigma–Aldrich Pty Ltd. was used for these depositions. The cooling of the 25 mm × 25 mm × 1 mm glass substrates to 6 °C was achieved by using a Peltier Thermoelectric Cooler. Prior to deposition, the chamber was evacuated to 1×10^{-5} Torr. The substrate was held intimately on the Peltier cooler which was placed on a slider that permitted an easy adjustment of the source–substrate distance along the line of sight from the evaporation source. High purity argon gas was back filled. Deposition of all films was carried out at 3×10^{-4} Torr, and the deposition rate was around 7.2 nm/min. A quartz crystal thickness monitor was used to measure the thickness and all the samples were deposited to a thickness of 200 nm as registered by the quartz crystal thickness monitor at a fixed distance of 25 cm. All the films were deposited under the same conditions except for the source–substrate distance. Post deposition heat treatment of the films was carried out in order to improve the density and stability of the deposited films. All samples were annealed at 400 °C in air for 1 h. The microstructural characterization was carried out using an atomic force microscope AFM (Dimension 3100 series, Digital Instruments) with VT102 vibration isolation table. The optical transmittance measurements were carried out using a Cary 5000 UV-Vis-NIR Spectrometer in the wavelength range between 200 and 2500 nm. An in-house built transmission/reflection ellipsometer was used to determine the optical constants n and k as well as the thickness of our samples. All the measurements were carried out between the angles of incidence of 10° and 70° at an interval of 10°. The optical constants (n, k) and the film thickness were obtained by fitting the experimental spectra with the theoretical model using, Optikan, an in-house developed thin film analysis software.

In order to examine the electrochromic behavior of the WO_3 samples, a dry method of lithium insertion developed in our laboratory was used [7]. High purity lithium niobate ($LiNbO_3$) powder was heated using a tungsten filament in a vacuum chamber to an optical temperature where through a decomposition, lithium atoms emanating from the source are inserted into the exposed WO_3 films. The thickness of the lithiation layer was monitored and controlled by a quartz crystal held near the substrate. It has been verified by the electrochromical method that the coloration under this insertion proceeds as shown in the reversible reaction above.

3. Results and discussion

Atomic force microscopy (AFM) was used to examine the surface topography of the samples and to determine the average roughness and the grain size for all samples. These results are shown in Fig. 1A for samples deposited at different source–substrate

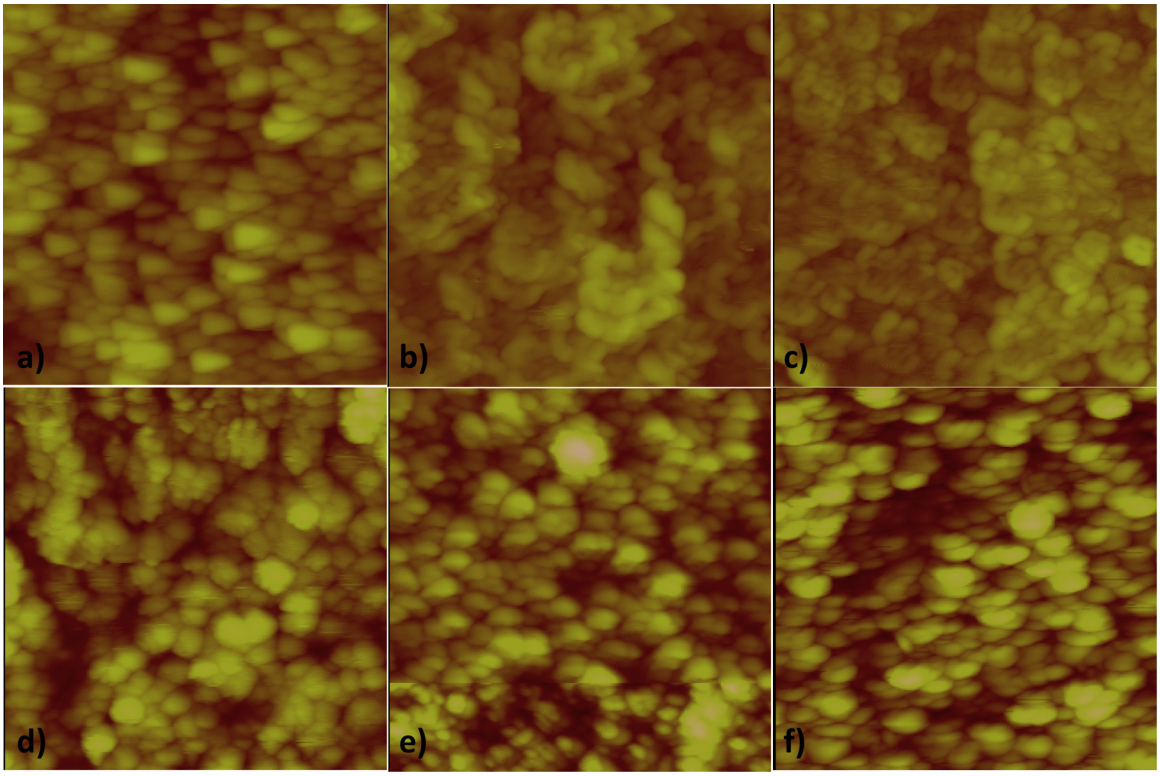

Fig. 1. AFM images of 1 μm × 1 μm dimension with a height range of 50 nm and source–substrate distances of: (a) 13 cm, (b) 15 cm, (c) 16 cm, (d) 18 cm, (e) 20 cm, and (f) 21 cm.

Please cite this article in press as: B. Abdel Samad, et al., Preparation of nanostructured tungsten trioxide thin films by high pressure sublimation and condensation, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.03.054

Download English Version:

https://daneshyari.com/en/article/5349176

Download Persian Version:

https://daneshyari.com/article/5349176

Daneshyari.com