Applied Surface Science xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Electrochromism of DC magnetron-sputtered TiO_2: Role of film thickness

Idris Sorar[a,b,*], Esat Pehlivan[c], Gunnar A. Niklasson[a], Claes G. Granqvist[a]

[a] Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden
[b] Department of Physics, Mustafa Kemal University, TR-31034 Antakya/Hatay, Turkey
[c] ChromoGenics AB, Märstagatan 4, SE-75323 Uppsala, Sweden

ARTICLE INFO

Article history:
Received 29 October 2013
Received in revised form 3 December 2013
Accepted 4 December 2013
Available online xxx

Keywords:
Electrochromism
Thin films
Titanium dioxide
Sputter deposition
Film thickness

ABSTRACT

Titanium dioxide films were prepared by reactive DC magnetron sputtering and the role of the film thickness d on the electrochromism was analyzed for $100 < d < 400$ nm. The best properties were obtained for the thickest films, which yielded a mid-luminous transmittance modulation of 58% and a corresponding coloration efficiency of 26.3 cm^2/C. The films were amorphous according to X-ray diffraction measurements and showed traces of adsorbed water as revealed by infrared spectroscopy.

1. Introduction

Electrochromic (EC) materials can be used in multilayer devices in order to modulate the optical properties, persistently and reversibly, so that a wide range of transmittance values are obtained [1]. These devices have numerous applications in optical technology and can be used for energy efficient and comfort enhancing windows in buildings [2–6]. A typical EC device for windows includes an EC film that changes color under charge insertion, another EC film that changes color under charge extraction, and an electrolyte – either a thin film or a polymer layer – joining these films; this three-layer stack is positioned between transparent electrical conductors. Optical modulation occurs when a voltage is applied between the transparent conductors so that charge is shuttled between the two EC films. Several of today's EC devices incorporate films of tungsten oxide and nickel oxide [6,7] but other alternatives, including titanium oxide, have attracted attention for many years.

Ti oxide colors under charge insertion (cathodically) and can replace W oxide. Recent work on the electrochromism of Ti-oxide-based materials has been reported for films and nanowire layers prepared by pulsed laser deposition [8], chemical vapor deposition [9] and spray pyrolysis [10], various chemical methods [11–14], anodization [15–17], and doctor blade technique [18,19]; the earlier literature was summarized in detail recently [20].

A previous investigation of sputter deposited electrochromic Ti oxide films [20] considered the influence of deposition parameters, specifically the sputter gas pressure, oxygen/argon ratio in the sputter plasma, and substrate temperature. In the present paper we report on a complementary study on the role of film thickness. Our films were prepared by reactive DC magnetron sputtering, which is a deposition technique that is well suited for large-area, large-scale manufacturing [21].

2. Experimental

The Ti oxide films were prepared by reactive DC magnetron sputtering in a deposition system based on Balzers UTT 400 vacuum unit. The films were deposited onto glass substrates pre-coated with indium tin oxide (In_2O_3:Sn, denoted ITO) with a sheet resistance of 15 Ω/square. The vacuum chamber was first pumped down to $\sim 10^{-7}$ Torr, and argon and oxygen (both 99.998% pure) were then introduced through mass-flow-controlled gas inlets. A 5-cm-diameter metallic Ti target (99.995% pure), positioned 13 cm from the substrate, was employed, and a constant current of 0.75 A was used to sustain the sputter plasma. Surface oxides on the Ti target were removed by pre-sputtering in argon plasma for five minutes, and pure oxygen was then admitted so that the pressure in the chamber was 25 mTorr and the oxygen/argon ratio was

* Corresponding author at: Department of Physics, Mustafa Kemal University, TR-31034 Antakya/Hatay, Turkey. Tel.: +90 326 245 5866; fax: +90 326 245 5867.
E-mail address: idrissorar@gmail.com (I. Sorar).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.12.015

0.04. The substrate temperature was kept constant at 25 °C, and the substrates were rotated during the depositions to assure film uniformity. Low substrate temperature and high gas pressure during sputtering are known to create a nanoporous film structure [22] that is conducive to electrochromism [23]. Every deposition took place under the same conditions to produce TiO_2 films, and the deposition time was set to obtain different values of the film thickness d. The deposition rate was calculated by dividing d with deposition time and was found to be ~11 nm/minute for all samples.

A Bruker Dektak XT surface profilometer was used to determine d. Film thicknesses were recorded for at least four different points on each sample, and individual values were averaged. The films reported on below had the thicknesses 102 ± 10, 181 ± 20, 291 ± 20 and 391 ± 20 nm.

We employed a Siemens D5000 X-ray diffractometer, operating with CuK_α radiation at a wavelength of 1.54 Å, to characterize the crystal structure of the TiO_2 films. A grazing incidence angle of 1° was used for diffraction angles between 20° and 60°. All TiO_2 films were found to be amorphous.

A Bruker Tensor 27 Fourier Transform (FT) instrument was used for film characterization by infrared (IR) spectroscopy. Measurements were done in the wavenumber range 500–4000 cm^{-1}. The resolution was 4 cm^{-1}, and each spectrum was averaged over 100 scans.

Spectral normal transmittance $T(\lambda)$ and reflectance $R(\lambda)$ in the $300 < \lambda < 2500$ nm wavelength range – encompassing luminous light at $400 < \lambda < 700$ nm – were recorded on a Perkin-Elmer Lambda 900 spectrophotometer equipped with a barium-sulfate-coated integrating sphere. The reflectance standard was a Spectralon plate.

Electrochemical measurements were performed with a Solartron 1286 electrochemical interface. A standard three-electrode cell configuration was used with a Ti oxide film serving as working electrode and Li foils as reference and counter electrodes. The electrolyte was 1 M $LiClO_4$ dissolved in propylene carbonate (PC). The Li^+ intercalation/deintercalation mechanism has been given as

$$TiO_2 + xLi^+ + xe^- \leftrightarrow Li_xTiO_2 \quad (1)$$

with e^- denoting electrons [1].

Cyclic voltammetry (CV) measurements were carried out with a scan rate of 20 mV/s in the potential range 1.0–3.2 V vs. Li/Li^+. Transmittance changes in the Ti oxide films due to charge insertion/extraction were measured in situ at a mid-luminous wavelength of $\lambda = 550$ nm by an Ocean Optics spectrophotometer. The films were positioned in an ultraviolet-transparent quartz cell. The 100%-level for the transmittance was recorded when the cell contained nothing but electrolyte. All electrochemical measurements were carried out under argon atmosphere in a glove box with <5 ppm water content.

The coloration efficiency η is a measure of the change in the optical properties per unit of charge insertion/extraction and should be as large as possible in a good EC device. This parameter was obtained from

$$\eta = \frac{ln(T_b/T_c)}{\Delta Q}, \quad (2)$$

where T_b and T_c are the transmittance values for films in bleached and colored states, respectively, and ΔQ is the corresponding inserted/extracted charge density.

3. Results and discussion

Fig. 1 shows FTIR data for Ti oxide films on glass substrates precoated with ITO and also for the bare substrate. A broad minimum is observed below 1000 cm^{-1}, which is consistent with Ti–O stretch modes in TiO_2 [24]. There is also a minimum around 3400 cm^{-1} for the film with $d = 291$ nm, and a weaker feature of the same nature is seen for $d = 181$ nm; these minima are related to O—H stretch modes in loosely bound water [24]. The minimum is shifted to around 3000 cm^{-1} for the film with $d = 391$ nm, probably because of overlap with interference effects.

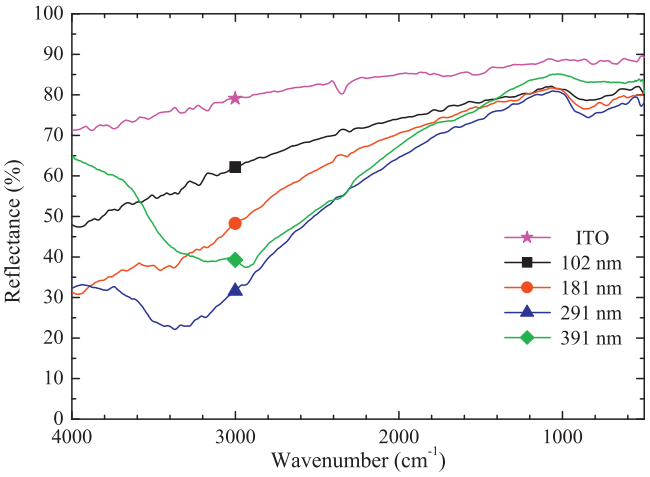

Fig. 1. FTIR spectra for Ti oxide films of various thicknesses deposited onto ITO-coated glass. Data are also given for the bare substrate.

Fig. 2 reports $T(\lambda)$ and $R(\lambda)$ for the same four Ti oxide films as in Fig. 1. All films have large transmittance in the luminous wavelength range. The IR reflectance is increased as a result of the ITO layer. Oscillations in the data are caused by optical interference.

Fig. 3 shows the 10th CV cycles of Ti oxide films with different thicknesses immersed in $LiClO_4$ in PC. The first scan began at 3.2 V vs. Li/Li^+ for the bleached state of the film. All samples reached good electrochemical reversibility already after the 3rd or 4th CV cycle. The data for the two thicker films show a consistent pattern with the cathodic current rising distinctly at ~2.3 V vs. Li/Li^+ and the anodic current having a broad maximum at ~1.7 V vs. Li/Li^+. Data for the thinnest and thickest films look somewhat different. A cathodic peak stands out at 1.23 V vs. Li/Li^+ for the thinnest film and an anodic current having a broad maximum at ~2.4 V vs. Li/Li^+ is observed for the thickest film.

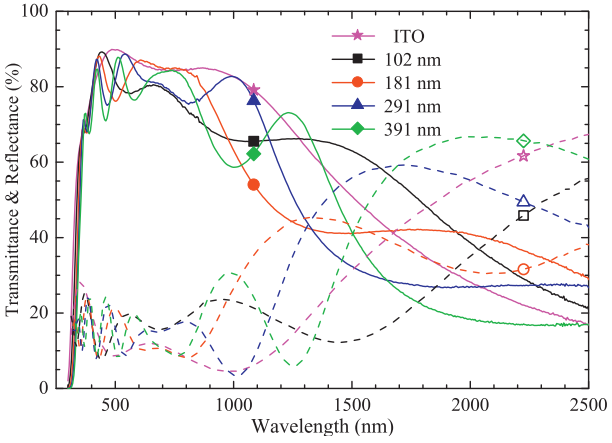

Fig. 2. Spectral transmittance and reflectance for Ti oxide films of various thicknesses deposited onto ITO-coated glass. Data are given also for the bare substrate. Solid curves and filled symbols refer to transmittance, dashed curves and open symbols refer to reflectance.

Please cite this article in press as: I. Sorar, et al., Electrochromism of DC magnetron-sputtered TiO_2: Role of film thickness, Appl. Surf. Sci. (2013), http://dx.doi.org/10.1016/j.apsusc.2013.12.015