Materials Science and Engineering B 165 (2009) 212–216

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Electrochromic TiO_2, ZrO_2 and TiO_2–ZrO_2 thin films by dip-coating method

T. Ivanova[a,*], A. Harizanova[a], T. Koutzarova[b], N. Krins[c], B. Vertruyen[c]

[a] Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, blvd. Tzarigradsko chaussee 72, Sofia, Bulgaria
[b] Institute of Electronics, Bulgarian Academy of Sciences, blvd. Tzarigradsko chaussee 72, Sofia, Bulgaria
[c] LCIS/SUPRATECS, Institute of Chemistry B6, University of Liege, Sart-Tilman, B-4000 Liege, Belgium

ARTICLE INFO

Article history:
Received 13 August 2008
Received in revised form 21 July 2009
Accepted 22 July 2009

Keywords:
Sol–gel deposition
Thin films
XRD
Electrochromic
Cyclic voltammetry

ABSTRACT

Sol–gel processing of TiO_2, ZrO_2 and mixed Ti/Zr oxide thin films has been studied as application of these coatings in electrochromic devices. Their structural transformations as a function of annealing temperatures were analyzed by XRD and FTIR techniques. Electrochromic behavior of the three kind materials was investigated by cyclic voltammetry and the basic electrochromic characteristics were determined.

1. Introduction

Electrochromism is defined as effect of the color change caused by applied electric field or voltage. The induced change in the optical absorption retains even when the excitation source is removed [1]. Electrochromic (EC) materials are exclusive interesting due to the variety of potential applications, including elements for information displays, antiglare rear-view mirrors, sunroofs and smart windows [2,3].

Nanostructured thin films with their porous structure facilitate increased mobility of the injected ions, and therefore are promising candidates for the enhancement of electrochromic properties. These films can be manufactured by sol–gel technology, which allows nanoscale morphology, porosity, smoothness and uniform surfaces of the resulting films [4,5]. The other advantage of sol–gel deposition is its ability to produce a wide range of materials including mixed oxide films with easy controlling their properties, thickness [6].

Titanium dioxide possesses high refractive index, chemical stability and high dielectric constant. The anatase TiO_2 exhibits a promising behavior as electrochromic material [7]. The anatase phase possesses tetragonal symmetry and is consisted from TiO_6 octahedras with two adjacent and shared edges, forming "zigzag" double chains. Vacant sites also form such rows, which are large enough to accommodate ions such as H^+ and Li^+.

Counter electrode is a very essential part of EC device. It must satisfy the following requirements such as reversible storage of a proper charge under the form of injected ions; to be transparent in the spectral range of the device application; upon ion intercalation and deintercalation to act as optically passive or to exhibit electrochromic effect in a sense opposite to that of working EC electrode and to be stable during long term cycling [8]. Optically passive counter electrodes can be ion storage materials with a large charge capacity and a high transparency. So far, these favorable properties have never been approached by a single stoichiometric compound. For example, CeO_2 is highly transparent, but possesses very low charge capacity. The mixed oxides based on cerium oxide reveal excellent transparency in the visible spectrum and during the intercalation/deintercalation cycles these oxide films are not influenced by the alkali ions and do not change their optical transmittance. Recently, the thin films of ZrO_2–TiO_2–CeO_2 [9] and $CeTi_2O_6$ [10] are investigated as counter electrodes in EC cells.

In this work, the sol–gel deposited TiO_2, ZrO_2 and mixed coatings are studied with respect to their application as electrochromic materials. The obtained thin films were structurally analyzed by XRD and FTIR spectroscopy. The electrochromic properties were monitored by the means of cyclic voltammetry and their electrochromic characteristics were determined.

2. Experimental

The formation of titanium dioxide [11] and zirconium dioxide sols were performed by using titanium ethoxide and zirconium propoxide as precursors at room temperature. Anhydrous ethanol

* Corresponding author. Fax: +359 2 875 40 16.
E-mail address: tativan@phys.bas.bg (T. Ivanova).

0921-5107/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2009.07.013

was used as solvent. The introduction of acetic acid caused an exothermic reaction. Gelation was obtained by adding a small amount of water. Acetylacetone was used as a peptizing agent.

Mixed oxide system was obtained by mixing equal molar parts of the two solutions and aged for a week. During this week, the mixed solution was treated at temperature of 40 °C in ultrasonic bath. The three solutions possessed clear and transparent appearances. They were found to be with the high stability up to 2 year without changing of their film forming properties.

Uniform coatings of TiO_2, ZrO_2 and TiO_2–ZrO_2 have been obtained by dipping in the colloidal solutions (with the withdrawal speed around 10 cm min^{-1}) on Si, glass and conductive glass substrates. After drying at 80 °C, the films were annealed at different temperatures in the range of 300–600 °C in air. The temperature was increased with the rate of 10 °C min^{-1} and cooling rate of 20–25 °C min^{-1}, respectively.

FTIR measurements were performed in the spectral region 350–1600 cm^{-1} by Shimadzu FTIR Spectrophotometer IRPrestige-21. XRD spectra of sol–gel thin films were recorded by means of XRD diffractometer Bruker D8, at the grazing angle 2° and step time 8 s and step 0.1°.

Electrochromic behavior was examined by cyclic voltammetry technique, performed in a standard three-electrode cell arrangement. The cell was consisted of Pt as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode. The electrodes were immersed in electrolyte of 1 mol/l $LiClO_4$ in propylene carbonate (PC). The color change was detected by optical system chopped light source and lock-in amplifier, attached to the cyclic voltammetry equipment. The current, the passed charge and the light transmittance were measured as a function of applied voltage at different wavelengths. Current density vs. voltage voltammograms were registered between −1.5 V and +1 V at different scanning rates ranging from 5 to 100 mV/s. Simultaneously the values of current (I) and charge (Q) are measured in dependence on applied voltage.

Color efficiency (CE) experimentally qualifies the modulation of the optical properties of electrochromic materials. It must be pointed out that color efficiency is spectrally dependent, and comparison is possible only for CE values obtained for one and same wavelength.

3. Results and discussions

Fig. 1 presents the recorded XRD patterns of sol–gel obtained zirconia treated at different temperatures. XRD spectra of ZrO_2 thin films revealed that the crystallization began at the lowest annealing temperature of 400 °C. Increasing of temperature leads to sharpen the XRD peaks and appearance of some new weaker lines (located at $2\theta = 38.5, 45, 59$). All detected XRD lines are assigned to tetragonal ZrO_2 crystal modification [12].

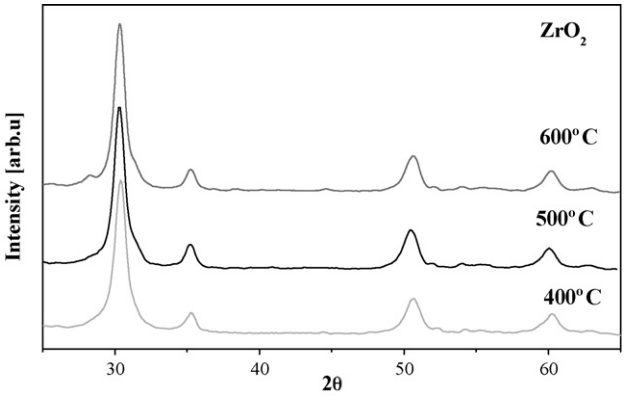

Fig. 1. XRD spectra of sol–gel ZrO_2 films, treated at different temperatures.

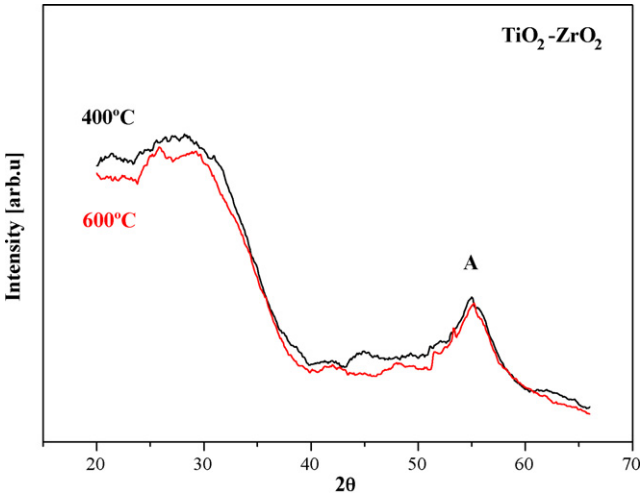

Fig. 2. XRD spectra of sol–gel TiO_2–ZrO_2 films, treated at different temperatures.

The lattice parameters are determined. The lattice parameters are $a = 4.343$ Å and $b = 3.122$ Å for sample, treated at annealing temperature of 400 °C. After 600 °C, the films are fully crystallized in tetragonal phase with lattice parameters $a = 5.594$ Å and $b = 2.98$ Å. The sizes of crystallites are estimated by using the Scherer formula. It is observed that the crystallites become bigger after higher annealing treatment, but still their dimensions are nanosized. The crystallite size of 400 °C annealed film is 6 nm, increasing to 9 nm for 500 °C and 10 nm for zirconium oxide film annealed at 600 °C. The annealing procedure is accomplished in oxygen atmosphere, which induces additional oxidation of the film and respectively more stoichiometric oxide matrix.

Our previous study [11] of sol–gel TiO_2 films showed that their crystallization began at the temperature above 450 °C in anatase phase. The anatase crystal modification is reported as suitable for electrochromic applications [7].

XRD spectra of TiO_2–ZrO_2 films are shown in Fig. 2. It can be seen that mixing the two oxides in a system (molar ratio 1:1) results in thin films that remain amorphous even after thermal treatment at 600 °C as observed from XRD measurements (it must be noted that intensity axis is extended five times in comparison to Fig. 1). The broad peak at $2\theta = 55$ can be related to anatase titania [13]. A broad feature located in the range $2\theta = 20$–33 might be a overlapping of XRD lines, as there are cited the most intensive XRD lines (tetragonal ZrO_2 and anatase TiO_2). The line shapes clearly indicate predominantly amorphous films. This is an interesting result as it is known that amorphous structure favors intercalation and deintercalation of small ions into film structure [14].

FTIR spectra of dip-coating films of ZrO_2, TiO_2 and ZrO_2–TiO_2 annealed at three temperatures of 400, 500 and 600 °C are given in Fig. 3.

Pure zirconium oxide films show a strong absorption band around 432 cm^{-1} after annealing at 400 and 500 °C and it is shifting towards 454.7 cm^{-1} for annealed film at 600 °C. These bands are indicative for tetragonal phase [15]. At the highest annealing temperature, an additional peak appears at 582.5 cm^{-1} assigned to tetragonal phase as well [15]. IR study suggests that ZrO_2 undergoes crystallization at relatively low temperatures (400 °C) in tetragonal crystal modification. Increasing the annealing temperature leads to better crystalline film structures. This conclusion confirms XRD analysis.

Titanium oxide films reveal IR lines related to anatase crystalline phase even after 400 °C annealing. The IR spectrum for TiO_2 film, treated at 600 °C presents two absorption lines located at 430 and