Electrochromic properties of heat-treated thin films of CeO$_2$–TiO$_2$–ZrO$_2$ prepared by sol–gel route

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Abstract

CeO$_2$–TiO$_2$–ZrO$_2$ thin films were prepared using the sol–gel process and deposited on glass and ITO-coated glass substrates via dip-coating technique. The samples were heat treated between 100 and 500 °C. The heat treatment effects on the electrochromic performances of the films were determined by means of cyclic voltammetry measurements. The structural behavior of the film was characterized by atomic force microscopy and X-ray diffraction. Refractive index, extinction coefficient, and thickness of the films were determined in the 350–1000 nm wavelength, using nkd spectrophotometry analysis.

Heat treatment temperature affects the electrochromic, optical, and structural properties of the film. The charge density of the samples increased from 8.8 to 14.8 mC/cm^2, with increasing heat-treatment temperatures from 100 to 500 °C. It was determined that the highest ratio between anodic and cathodic charge takes place with increase of temperature up to 500 °C.
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1. Introduction

Mixed cerium oxide and titanium oxide are recognized as passive counter electrodes in electrochromic devices [1–4]. The ion storage capacities of such films are sufficiently high enough to drive the coloring of tungsten oxide films, and exhibit relatively high transparency in the bleached state [5]. Zirconium oxide, by itself, is not able to intercalate lithium. The process is related to the oxidation/reduction of cerium in mixed cerium–zirconium oxide [6]. Veszelei et al. [7] demonstrated that Ce–Zr mixed oxide films had a high charge capacity during the first voltammetric sweeps and were fully transparent over the whole visible range. Vassano et al. [6] showed that Ce–Zr mixed oxide exhibits favorable optical properties in its use as a passive electrode in electrochromic devices (high transparency in the visible spectrum in the oxidized and reduced state). Avellaneda et al. [8] prepared a counter-electrode

layer of CeO$_2$–TiO$_2$–ZrO$_2$ composition with 23 mol% of Ce, 45 mol% of Ti, and 32 mol% of Zr. They obtained the optical and electrochemical properties of sol–gel films that they made. It was found that CeO$_2$–TiO$_2$–ZrO$_2$ lithium-doped sol–gel films exhibit an improved reversibility during insertion/extraction processes. In this work, the effect of heat treatment on the electrochromic structural and optical properties of sol–gel derived CeO$_2$–TiO$_2$–ZrO$_2$ thin films— prepared by dip-coating method with a mole ratio of 50 mol% of Ce, 25 mol% of Ti, and 25 mol% of Zr—was studied.

2. Experimental

2.1. Film preparation

The CeO$_2$–TiO$_2$–ZrO$_2$ thin films were prepared using the sol–gel process. The films were deposited on Corning 7059 glass (barium borosilicate) substrates using the dip-coating technique at a pull rate of 107 mm/min. The samples were dried for approximately 1 h at 100 °C; this process was

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repeated three times. Heat treatment was applied onto the samples inside a temperature-controlled furnace at 100, 300, and 500 °C for 1 h, heated up at a ramp rate of 60 °C/h. In the preparation of the ternary sol, ceric ammonium nitrate was used as the main precursor. It was added to ethanol and stirred for 30 min by a magnetic stirrer. Titanium butoxide and zirconium propoxide (with a mole ratio of 0.50 0.25, 0.25 for Ce, Ti, and Zr, respectively) were added to the mixture separately. The mixture was stirred for 30 min. Small amounts of acetic acid and distilled water were added to the mixture to accelerate hydrolysis and condensation. Homogenous transparent solution was obtained by stirring the mixture for 24 h. In order to attain a high transparent coating, the Ce–Ti–Zr mixed oxide solution was aged for 8 days at room temperature (16 ± 3 °C) with a humidity of (50 ± 5%). Within a few days, the color of the solution changed from a deep red to a pale yellow, indicating a reduction of cerium (IV) by ethanol [2]. Fig. 1 illustrates the flow chart of the CeO_2–TiO_2–ZrO_2 coating process.

2.2. Film characterization

X-ray diffraction (XRD) analyses of the CeO_2–TiO_2–ZrO_2 thin films deposited on glass substrates were obtained using a PHILIPS PW-1840 diffractometer—the diffractometer is equipped with a Cu rotating anode and a monochromator for sample irradiation and detection of the Cu K_α radiation scattered from the sample surface.

Cyclic voltammetry was performed using a high-power Wenking potentiostat (Model Hp 88, Bank Electronic), in the voltage range of -1.5 to $+1.5$ V, versus Pt in a three-electrode cell. A potential scan rate of 50 mV/s was used for cycling voltammetry.

An Aquila 7000 nkd spectrophotometer was used to measure the optical transmittance and reflectance of the CeO_2–TiO_2–ZrO_2 thin films. The refractive index, extinc-

tion coefficient, and thickness of the films were calculated by Pro-Optix software, by the fitting of measured data into a Cauchy model.

Detailed morphological analysis of the CeO_2–TiO_2–ZrO_2 thin films was carried out using a scanning probe microscope (Model SPM-9500, Shimadzu Corp.).

3. Results and discussion

XRD studies of CeO_2–TiO_2–ZrO_2 thin films coated on glass substrates, and heat-treated at 100, 300, and 500 °C for 60 min, are represented in Fig. 2. The XRD patterns demonstrate that the films heat-treated at 100 and 300 °C exhibit mainly amorphous structure and do not exhibit
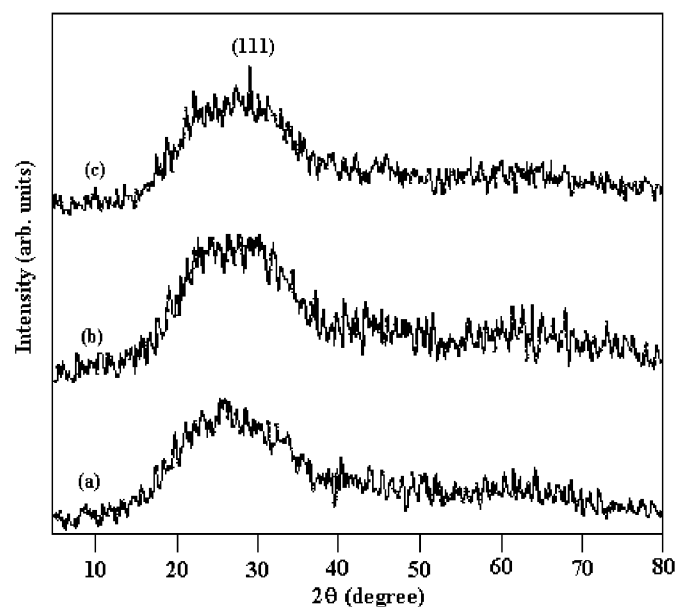
Fig. 2. X-ray diffraction patterns of sol–gel derived CeO_2–TiO_2–ZrO_2 thin films heat treated at (a) 100, (b) 300, and (c) 500 °C.
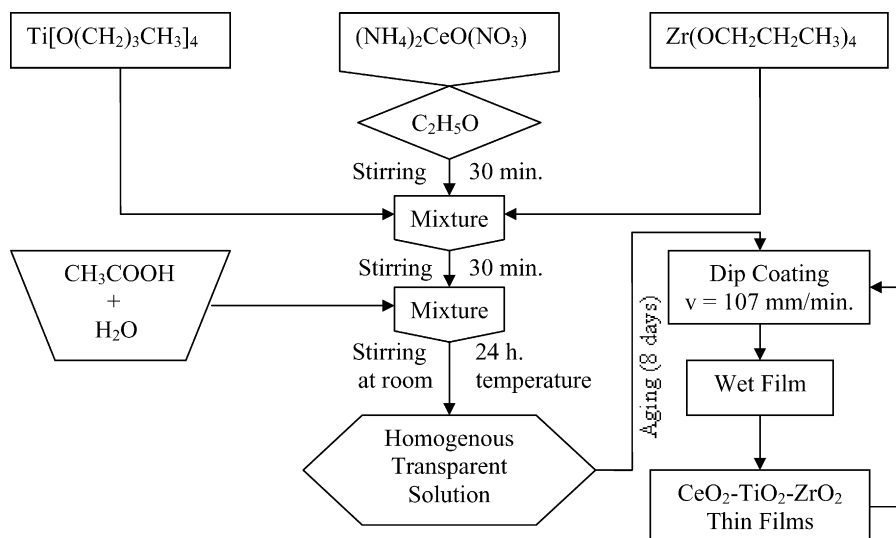
Fig. 1. Flow chart of sol–gel derived CeO_2–TiO_2–ZrO_2 coating process.

peaks of crystalline phases of CeO_2, TiO_2, and ZrO_2. In regards to the films heat-treated at 500 °C, the pattern exhibits an amorphous structure with a small amount of crystalline phase as a result of a low (1 1 1) diffraction line—revealed in the pattern corresponding to the CeO_2.

Fig. 3(a)–(c) illustrates the atomic force microscopic images (AFM) of three different films deposited on corning glass substrates and heat treated at 100, 300, and 500 °C for 60 min. The surfaces of dip-coated films appeared to be crack free on the explored section (in $5 \times 5\,\mu m^2$ area) and exhibited a better homogeneity in thickness when the heat treatment temperature was increased. The roughness in the films' thickness decreases from about 8.5 to 3.6 nm (in RMS) when the temperature was increased from 100 to 500 °C. This effect lessened after 300 °C and showed reduction of densification above 300 °C. In films heat-treated below 300 °C, the amount of organic compound is important to the pore walls. If the amount of organic compound is low enough at high temperatures, the importance of the organic compound is lessened. This effect converts the electrostatic attraction between the OH dipoles to repulsion. Thus, densification of the films lessens above 300 °C.

Fig. 4(a)–(c) represents typical results of cyclic voltammetry (CV) measurements in the potential window between -1.5 and 1.5 V, versus Hg/HgSO$_4$ electrode in LiClO$_4$/PC anhydrous electrolyte. The CV measurements show that the samples heat-treated at 100, 300, and 500 °C exhibit an anodic charge density of 2.72, 4.86, and 7.19 mC/cm^2, respectively. The sample heat-treated at 300 and 500 °C

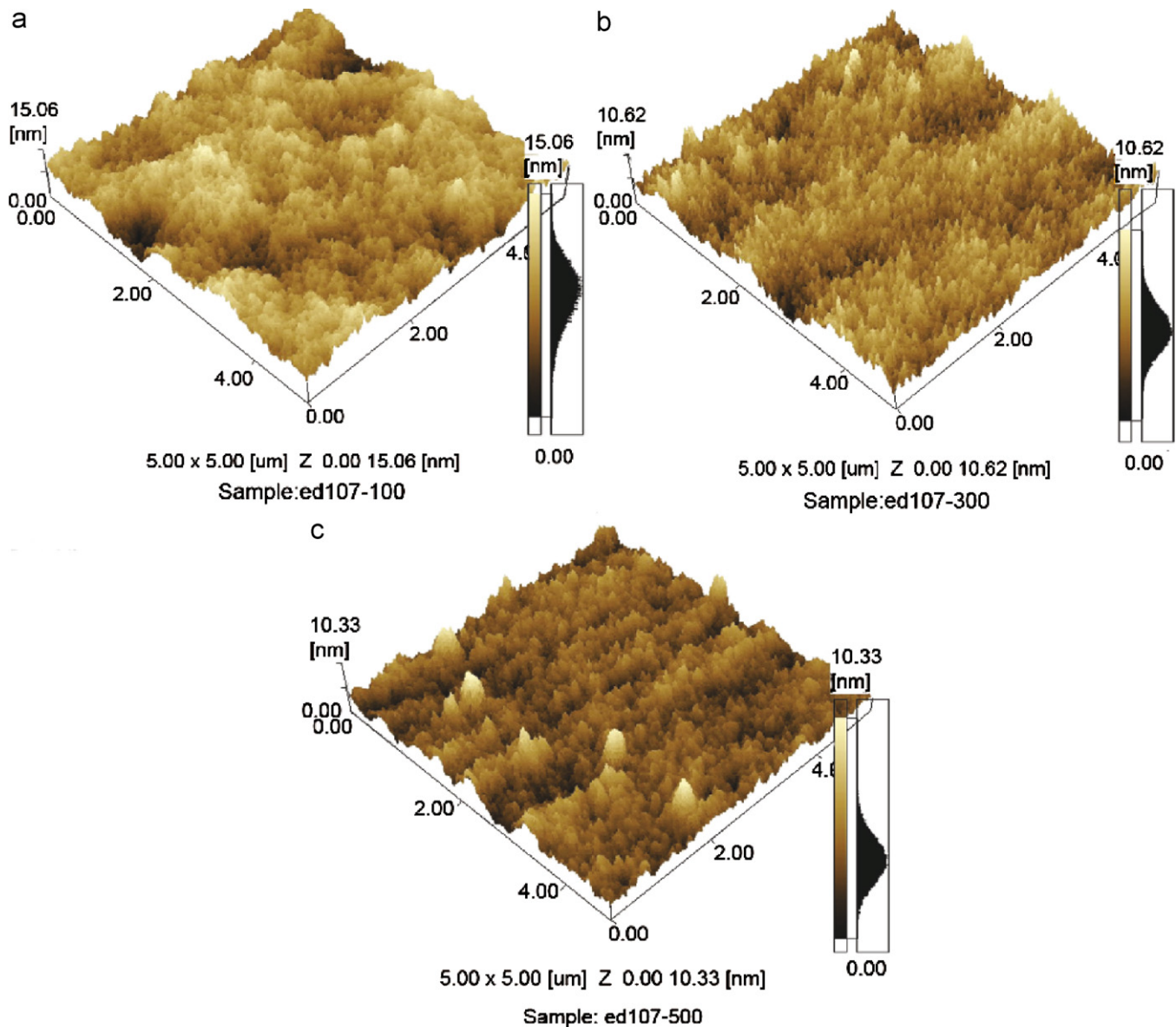Fig. 3. Atomic force microscopy images of the CeO_2–TiO_2–ZrO_2 thin films deposited on glass substrates and heat treated at (a) 100, (b) 300, and (c) 500 °C.
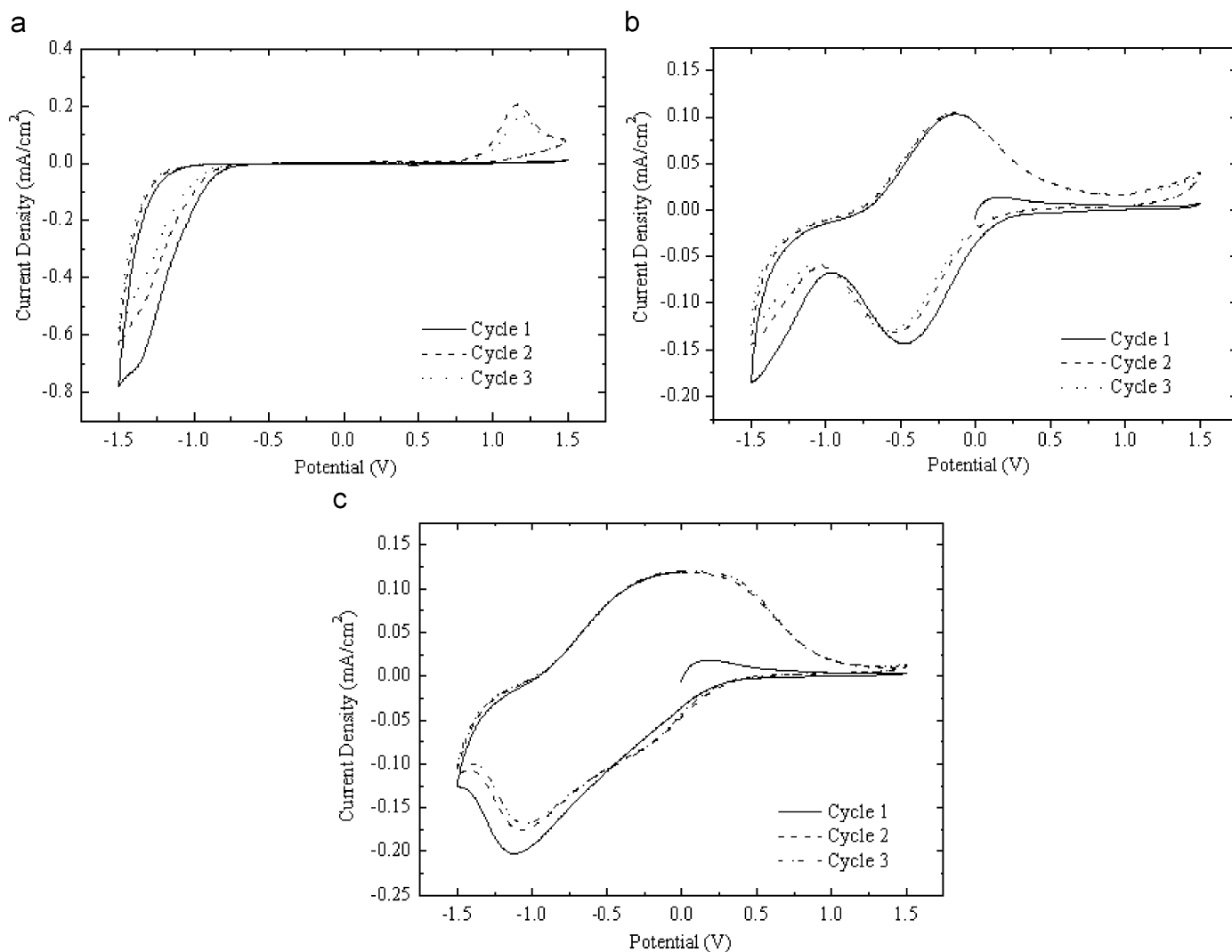
Fig. 4. Cyclic voltammograms of CeO_2–TiO_2–ZrO_2 thin films deposited by dip-coating technique and heat-treated at (a) 100, (b) 300, and (c) 500 °C (in 1 M $LiClO_4$/PC anhydrous electrolyte, with a $Hg/HgSO_4$ reference electrode).

exhibits well-defined reduction and oxidation peaks. The shape of voltammograms changes with heat-treatment temperature. The anodic peak at 1.25 V versus $Hg/HgSO_4$ shifts to the lower values and broadens for the sample heat-treated at 500 °C. The current that passes through the electrode decreases with the increasing of heat-treatment temperature from 100 to 500 °C. The ratio between anodic and cathodic charge insertions is 0.45, 0.83, and 0.95 for the same condition. The results show that the sample annealed at 500 °C has better reversibility with respect to the samples heat treated at 100 and 300 °C. This fact indicates better stability for the samples annealed at 500 °C.

Spectral transmittance and reflectance of CeO_2–TiO_2–ZrO_2 thin films, heat-treated at 100, 300, and 500 °C are shown in Fig. 5(a) and (b). Increasing the heat-treatment temperature decreases the transparency of the films, while increasing their reflectance. Incremental increases of heat-treatment temperature results in a reduction of roughness, with a homogeneity in thickness. As a result, the reflection

of the electromagnetic beam will be in nearly the same direction in spite of random scattering. In this case, the reflectance increases. Decrease of transparency is a result of the film densification and the reduction of pores sizes. All the sol–gel derived films, deposited by the dip-coating technique and annealed at different temperatures, are transparent in the visible region of the spectra.

The dispersion of refractive index, extinction coefficient, and thickness of CeO_2–TiO_2–ZrO_2 thin films were calculated from reflectance and transmittance spectra in the range of 300–1000 nm using Pro-Optix software, which fits measured data to a Cauchy model. The refractive index and extinction coefficient of CeO_2–TiO_2–ZrO_2 thin films, heat-treated at 100, 300, and 500 °C for 60 min, are represented in Figs. 6 and 7, respectively. The refractive index and extinction coefficient of the sample increases with an increase in heat-treatment temperature. This results from an increasing densification of the films and a rising of packing density with heat-treatment temperatures.
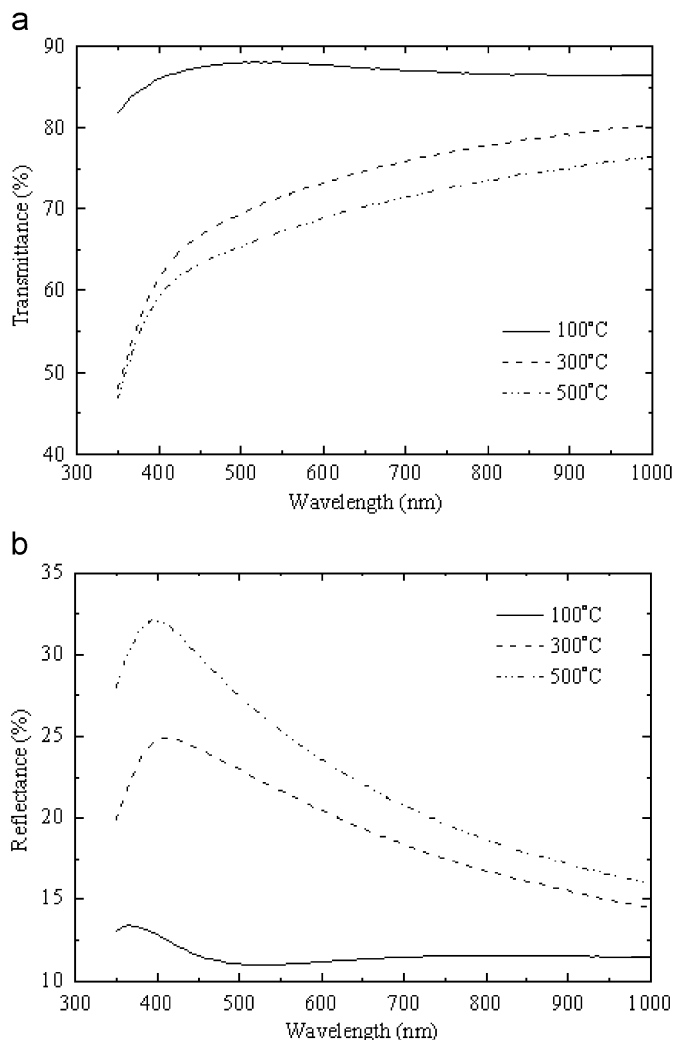
a

b

Fig. 5. Spectral (a) transmittance and (b) reflectance of the CeO_2–TiO_2–ZrO_2 thin films deposited by dip-coating technique and heat-treated at different temperatures.

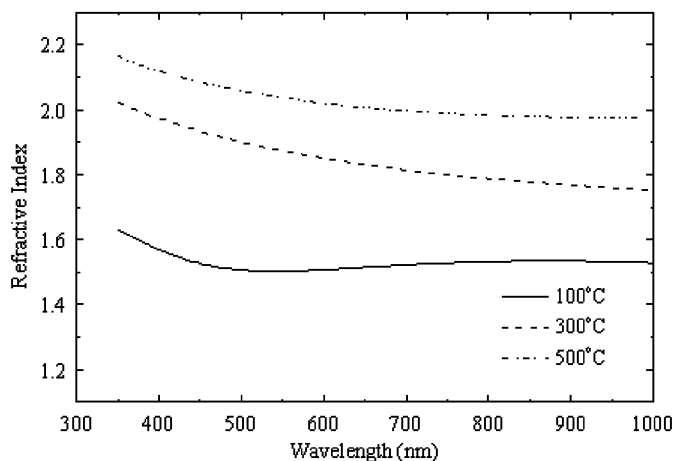Fig. 6. The refractive index dispersion for the CeO_2–TiO_2–ZrO_2 thin films deposited by dip-coating technique and heat-treated at different temperatures.
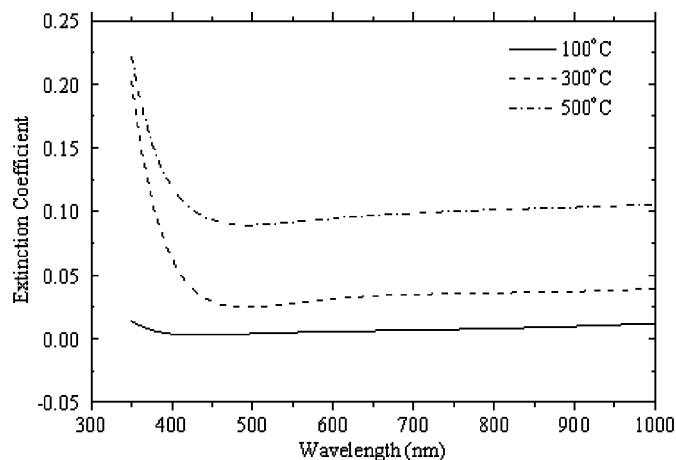

Fig. 7. Wavelength dependence of extinction coefficient for the CeO_2–TiO_2–ZrO_2 thin films deposited by dip-coating technique and heat-treated at different temperatures.

4. Conclusion

Electrochromic, structural, and optical properties of sol–gel-made CeO_2–TiO_2–ZrO_2 thin films—with a mole ratio of 50 mol% of Ce, 25 mol% of Ti, and 25 mol% of Zr heat-treated at 100, 300, and 500 °C temperature—have been investigated. XRD patterns exhibit an amorphous structure for all samples, except the sample heat-treated at 500 °C, which exhibits a small amount of crystalline phase corresponding to the CeO_2. AFM images show that the roughness of the sample decreases with an increase of heat treatment temperature. Sol–gel derived CeO_2–TiO_2–ZrO_2 thin films prepared by this method showed an improved reversibility during the insertion/extraction processes. The charge density of the film heat-treated at 500 °C was found to be 14.8 mC/cm^2 and exhibited the best electrochemical reversibility among the studied films.

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