Optical and structural properties of sol–gel made Ce/Ti/Zr mixed oxide thin films as transparent counter electrode for electrochromic devices

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Abstract

Ce/Ti/Zr mixed oxide thin films were prepared using sol–gel process with mole ratios from 45/5 to 5/45 of Ti/Zr and 50 of Ce and deposited by dip coating technique. Optical, electrochromic, and structural properties of such films were investigated. The thickness, refractive index, and extinction coefficient of the films were calculated through transmission and reflection measurement by an nkd spectrophotometer. The surface morphology and structural behaviors of the films were characterized by atomic force microscopy and X-ray diffraction. Cyclic voltammetry measurements also were used to study electrochromic properties of these films. The best counter electrode Ce/Ti/Zr oxide thin film is achieved for the sample with a mole ratio of 40/10 of Ti/Zr. The ratio between anodic and cathodic charge is about 0.95 for this sample with a surface roughness of 1.8 nm.
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1. Introduction

Several attempts have been made in order to improve optical and electrochromic properties of CeO_2, mixed CeO_2–TiO_2, and CeO_2–ZrO_2 as ion storage layer in electrochromic devices [1–5]. Recently, sol–gel derived CeO_2, TiO_2, and CeO_2–TiO_2 thin films have been studied for use as thin film semiconductor oxide in solar cell application [6].

In the last decades, CeO_2 has been investigated as passive counter electrode due to its high transparency in both the oxidized and reduced state [7,8]. However, the response times of such films have been too low compared to WO_3 films [3].

CeO_2–TiO_2 and CeO_2–ZrO_2 have been prepared by several methods such as physical vapour deposition [9], dc magnetron sputtering [10,11], sol–gel [12–14], and spray technique [15]. They studied the best ranges of compositions, deposition conditions, and aging time for application to smart windows, oxygen gas sensing, and UV absorbent coatings. To our knowledge there are a few investigations concerning the optical and electrochromic behavior of the CeO_2–TiO_2–ZrO_2 thin films [16,17]. We also investigated the electrochromic properties of heat-treated thin films of CeO_2–TiO_2–ZrO_2 prepared by sol–gel route [18].

In the present paper, we report on the optical, electrochromic, and structural properties of sol–gel derived Ce/Ti/Zr mixed oxide thin films with various Ti/Zr ratios from 45/5 to 5/45 deposited by dip coating technique. The films were characterized by nkd spectrophotometry, atomic force microscopy, X-ray diffractometry, and cycling voltammetry analysis.

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2. Experimental

2.1. Film preparation

Mixed Ce/Ti/Zr oxide thin films with various Ti/Zr ratios have been prepared by the sol–gel process. The films were deposited on Corning glass substrates by using the dip coating technique with a pulling rate of 107 mm/min. For preparation of samples, the Corning glass substrates were cleaned with detergent and de-ionized water carefully and washed with de-ionized water using a Bandeline Sonorex RK-100 ultrasonic cleaner. Finally, the substrates were cleaned with a mixture of ethanol and acetone and dried at 60 °C for 30 min.

The main precursor ceric ammonium nitrate was dissolved into ethanol and stirred by magnetic stirrer for 30 min. Appropriate stoichiometric amount of titanium butoxide, and zirconium propoxide added into mixture separately. The mixture was stirred for 30 min. A small amount of acetic acid and distilled water were added to the mixture to accelerate hydrolysis and condensation. The mixture was stirred for 24 h. Homogenous deep red transparent solution was achieved. The solution was aged for 8 days. The colour of the solution was turned from deep red to pale yellow in a few days indicating a reduction of cerium (IV) by ethanol.

The prepared solution with various Ti/Zr ratios have been dip coated onto cleaned Corning glass substrates (for optical and morphological measurements) and ITO (indium tin oxide) coated substrates (for cyclic voltammetry measurements) with a pulling rate of 107 mm/min. and dried for about 1 h in a furnace at 100 °C. The compositions of the prepared samples are given in Table 1. The coating process was repeated for three times.

2.2. Film characterization

The optical transmittance and reflectance of mixed Ce/Ti/Zr oxide thin films have been carried out by an Aquila

Table 1
The ratios of Ti/Zr in the compositions, refractive index (n), extinction coefficient (k), thickness (d), roughness (R), total and anodic ion storage capacity (Q_t and Q_a), and the anodic–cathodic ion storage ratio (Q_a/Q_c) of Ce/Ti/Zr oxide thin films. The optical constants determined at $\lambda = 550$ nm

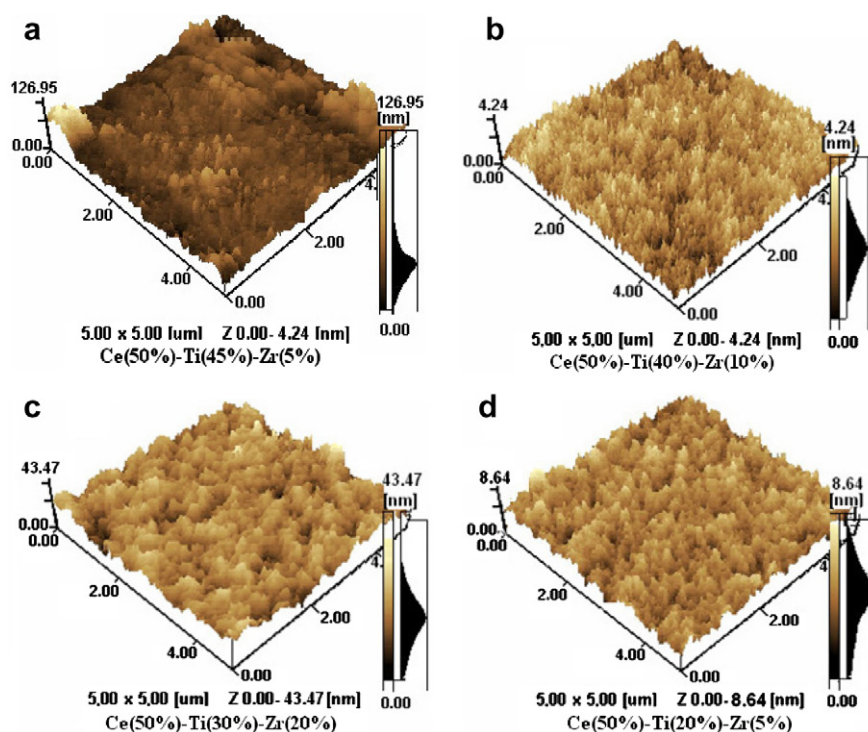| Sample	Ti (%)	Zr (%)	n	k	d (nm)	R (rms) (nm)	Q_t (mC/cm^2)	Q_a (mC/cm^2)	Q_a/Q_c
1	45	5	1.639	0.0353	76.0	22.5	5.33	2.16	0.681
2	40	10	1.528	0.0103	109.5	1.8	10.2	4.97	0.950
3	30	20	1.571	0.0605	90.7	19.4	7.54	2.38	0.461
4	25	25	1.514	0.0049	80.8	7.3	8.77	2.72	0.450
5	20	30	1.510	0.0152	123.0	4.0	10.9	3.99	0.577
6	10	40	–	–	–	–	12.6	4.19	0.498
7	5	45	–	–	–	–	18.4	7.92	0.756

Fig. 1. Comparison of AFM images of Ce/Ti/Zr oxide thin films with the mole ratios of (a) 45/5, (b) 40/10, (c) 25/25, and (d) 20/30 of Ti/Zr in the composition.

6000 nkd spectrophotometer at an angle of incidence of 60°. The refractive index, extinction coefficient, and thickness of the films evaluated by Pro-Optix software by fitting of measured data to Cauchy model [19]. In order to study the surface morphology and fine scale microstructure of Ce/Ti/Zr oxide thin films, atomic force microscopy (AFM) analysis was performed using a Shimadzu scanning probe microscope. XRD analyses of the films deposited on glass substrates were carried out on a PHILIPS model PW-1840 diffractometer equipped with a Cu rotating anode and a monochromator for sample irradiation and detection of the radiation scattered from the sample surface. Cyclic voltammograms have been recorded using a High Power Potentiostat Wenking Model Hp 88 (Bank Electr.), between –1.5 and +1.5 V versus Hg/HgSO$_4$ in a three-electrode cell containing LiClO$_2$/PC anhydrous electrolyte. A potential scan rate of 50 mV/s was used for cycling voltammograms.

3. Results and discussion

The surface morphology of sol–gel derived mixed Ce/Ti/Zr oxide thin films with various compositions of Zr and Ti have been illustrated in Fig. 1. As can be seen, the roughness of surfaces varies when the ratio of Ti/Zr in composition changes. The films with mole ratios of 30/20 and 45/5 show more rough thickness with respect to other samples. It is found that the smoothest film in thickness was achieved with a mole ratio of 40/10. The XRD patterns show that the Ce/Ti/Zr oxide films were mainly amorphous and no peaks of any crystallite phase of CeO$_2$, TiO$_2$, and ZrO$_2$ were observed for the films prepared in this work.

The spectral behavior of the transmittance, and reflectance, at oblique incident of light in the range from 300 nm to 1000 nm of Ce/Ti/Zr oxide thin films with different ratio of Ti/Zr in the compositions are represented in
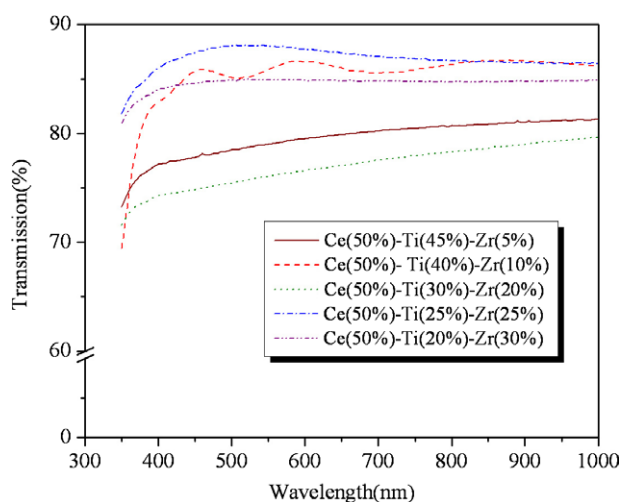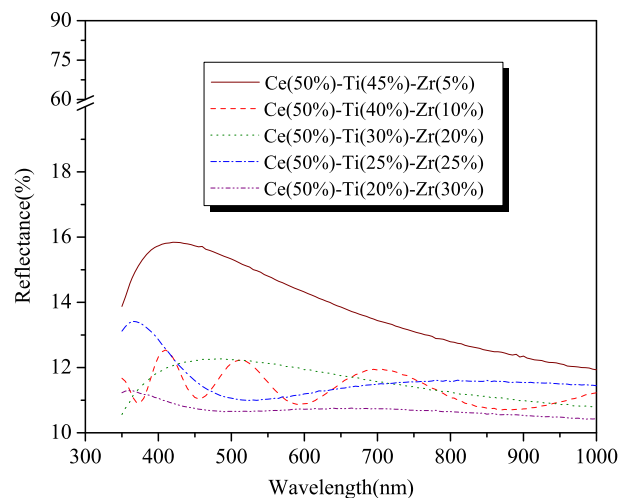

Fig. 3. Reflectance spectra of Ce/Ti/Zr oxide thin films with different ratio of Ti/Zr deposited by dip coating technique.

Figs. 2 and 3, respectively. The sample with a mole ratio of 40/10 shows the interference fringe in transmittance while the sample with a mole ratio of 30/20 shows in reflectance. However the films with mole ratios of 30/20 and 45/5 must be thicker than the film with a mole ratio of 40/10 but because of high roughness in the films with mole ratios of 30/20 and 45/5 the interference fringes of transmission were destroyed and the sample with a mole ratio of 40/10 shows interference fringes in transmission.

The refractive index of the Ce/Ti/Zr oxide thin films with various ratio of Ti/Zr in the compositions is shown in Fig. 4. The refractive index of the films varies as the mole ratio of Ti/Zr in composition changes. Their values rise near the absorption edge and follow Cauchy's formula [18]. The highest and lowest values of refractive index of the films in the visible region corresponds 45/5 and 20/30 mole ratios in composition, respectively. It means that

Fig. 2. Spectral transmission of Ce/Ti/Zr oxide thin films with different ratio of Ti/Zr in the compositions.
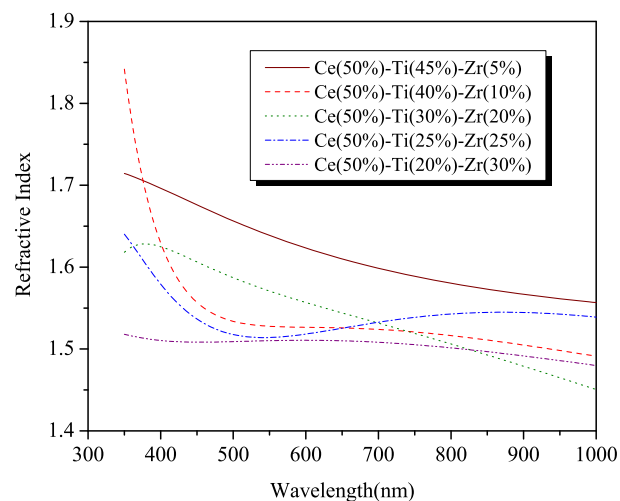

Fig. 4. Wavelength dependence for the refractive index for Ce/Ti/Zr oxide thin films deposited by dip coating technique with different ratio of Ti/Zr in the compositions.
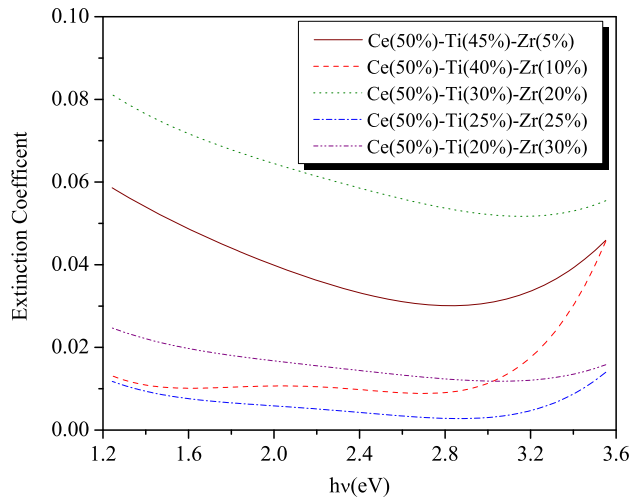
Fig. 5. Extinction coefficient of Ce/Ti/Zr oxide thin films with different ratio of Ti/Zr in the compositions.

the refractive index of the film increases as the content of Zr increases in the composition.

Fig. 5 shows wavelength dependence of extinction coefficient of the Ce/Ti/Zr oxide thin films with various ratio of Ti/Zr in the compositions. As can be seen in figure, extinction coefficient of the film varies when the ratio of Ti/Zr changes. The highest and lowest values of extinction coefficient of the films in the visible region are corresponding to 30/20 and 25/25 mole ratios in composition, respectively. These results show that the behavior of extinction coefficient is different from the behavior of refractive index with respect to variation of ratio of Ti/Zr in composition. It is evidence that indicates the structure of the films varies when the ratio of Ti/Zr changes in composition.

To obtain information about the role of ratio of Ti/Zr in redox processes, cyclic voltammetry of Ce/Ti/Zr oxide thin films deposited on ITO (Indium Tin Oxide) were carried out in the voltage range from –1.5 to +1.5 V versus Hg/HgSO$_4$ in a three-electrode cell containing LiClO$_2$/PC anhydrous electrolyte. Fig. 6 shows the third scan of cyclic voltammetries for sol–gel prepared Ce/Ti/Zr oxide thin films with various ratio of Ti/Zr in the compositions. The ion storage capacity of Ce/Ti/Zr oxide increases with
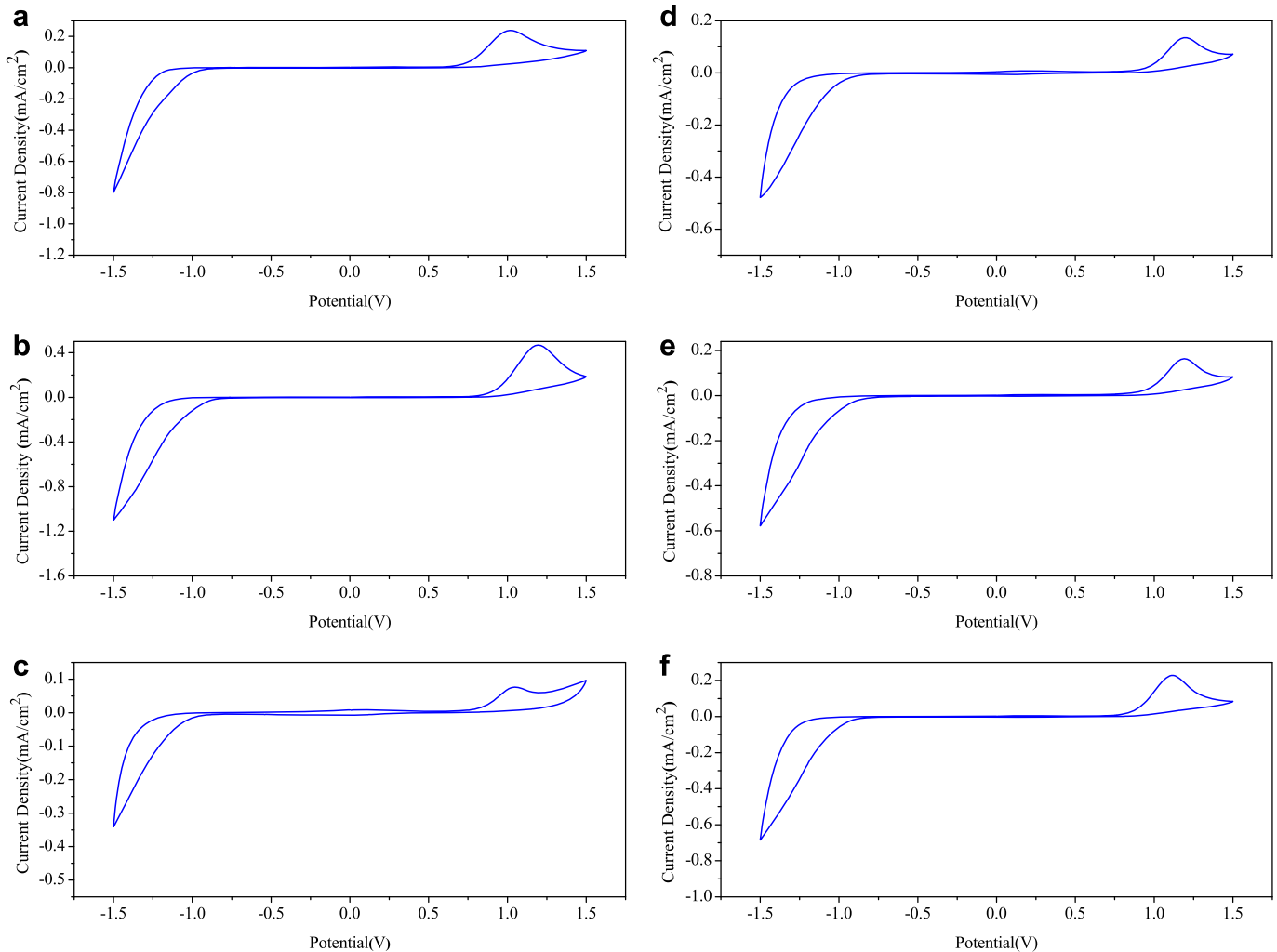

Fig. 6. Cyclic voltammograms of Ce/Ti/Zr oxide thin films deposited by dip coating technique with the mole ratios of (a) 45/5, (b) 40/10, (c) 30/20, (d) 25/25, (e) 20/30, and (f) 5/45 of Ti/Zr in the composition (in 1 M LiClO$_4$/PC anhydrous electrolyte, with a Hg/HgSO$_4$ reference electrode).

increasing the ratio of Zr in composition with an exception for the sample with 40/10 mole ratio of Ti/Zr. The lowest and highest ion storage capacities are corresponding to the sample with 45/5 and 5/45 mole ratios of Ti/Zr in composition, respectively.

The refractive index (n) and extinction coefficient (k) at 550 nm wavelength, thickness (d), roughness, total ion storage capacity (Q_t) and anodic (Q_a) ion storage capacity, and the anodic–cathodic ion storage ratio (Q_a/Q_c) of Ce/Ti/Zr oxide thin films with various ratios of Ti/Zr in the compositions are given in Table 1. The results show that the smoothest films achieved for the sample with a mole ratio of 40/10 of Ti/Zr in composition. The film thickness varied from 76 nm to 123 nm. The ratio between inserted and extracted charge (Q_a/Q_c)) improves from 0.45 to 0.95. One of the parameters extremely responsible on the total ion storage capacity is the thickness of the films. It can be seen from Table 1 that increasing of thickness of the films increases total ion storage capacity of the films approximately. On the other hands, the role of roughness of the films on the intercalation–deintercalation process is also important. The results show that the roughness of the films which is an evidence of existence of summits and valleys on the surface of the layer cause the ions deintercalation process be prevented by trapping the ions into the valleys. On the other hand, the summits on the surface cause scattering of ions and prevent the intercalation of ion into the layer.

4. Conclusion

Ce/Ti/Zr mixed oxide thin films with various ratios of Ti/Zr were prepared by using sol–gel process successfully. The Optical measurements show that the samples with the mole ratios of 25/25 and 30/20 have the highest and lowest transparency, respectively. Furthermore, the mole ratios of Ti and Zr in composition affect the refractive index, extinction coefficient, thickness, and surface roughness of the films. Ce/Ti/Zr mixed oxide thin films are good counter electrode for electrochromic devices. Their ion storage capacities are sufficiently high for electrochromic application. The results show that the best ion storage Ce/Ti/Zr mixed oxide thin films with smoothest surface

(with a roughness of about 1.8 nm) is achieved for the sample with a mole ratio of 40/10 of Ti/Zr.

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