Influence of pH on the optical and structural properties of spin coated CeO$_2$–TiO$_2$ thin films prepared by sol–gel process

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Abstract

Optical and structural properties of mixed CeO$_2$–TiO$_2$ thin films have been investigated by varying the pH of the coating sol. The films were prepared by sol–gel process using spin-coating technique with a spin speed of 2500 rpm. The optical and structural properties of films were examined by a spectrophotometer, AFM and XRD. Optical constants and thickness of the CeO$_2$–TiO$_2$ thin films have been determined with respect to the pH of the coating bath before deposition. The refractive index at 550 nm wavelength increases from 1.49 to 1.60 when the pH of the sol increases from 2.22 to 2.92. The thickness increases from 46.6 nm to 96.1 nm in this pH range. The XRD measurements show that the films have amorphous structure. The AFM analysis shows that the pH of sol prior to deposition changes the uniformity and porosity of the films.
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1. Introduction

The sol–gel process is ideally suited for preparation of optical materials particularly in thin film forms [1]. Optical and structural properties of the films can be tailored easily using sol–gel route [2–8]. It is possible to control these properties by changing the chemical and deposition conditions.

Over past decade, several researchers have worked on preparation and characterization of sol–gel derived CeO$_2$–TiO$_2$ thin films for optical and electrochromic applications [9–20]. Makishima et al. [9,10] investigated the preparation of dip-coated CeO$_2$–TiO$_2$ films with different alkoxyl group of titanium alkoxide and catalyst. They showed optical properties of the films depend on the number of layers. Electrochemical properties of dip-coated CeO$_2$–TiO$_2$ thin films were studied by Baudry et al. [11]. Keomany et al. [12,13] characterized various forms of

CeO$_2$–TiO$_2$ thin films by changing the mole rate of CeO$_2$ in the composition. Spectrochemical and SEM analysis of CeO$_2$ and mixed CeO$_2$–TiO$_2$ films have been examined by Stangar et al. [14] using dip coating technique. Tonazzi et al. [15] has studied the structure of sol–gel derived CeO$_2$–TiO$_2$ films by means of X-ray scattering measurements. Macrelli and Poli [18] have studied optical and electrochemical properties of mixed cerium/titanium and cerium/zirconium oxides as thin film counter electrodes prepared by electron beam reactive evaporation. They found that mixed Ce/Ti oxide is the most suitable material as optically passive counter electrode in the electrochromic system. DC magnetron sputter-deposited WO$_3$ and CeO$_{2-x}$–TiO$_2$ thin films have been investigated by Janke et al. [19] for electrochromic application. They examined the intercalation process of such films and showed that in case of the ion-storage layer, cerium oxide CeO$_{2-x}$ was the active part in inter- and deintercalation processes. Trinchi et al. [20] have studied the oxygen gas sensing performance of semi conducting CeO$_2$–TiO$_2$ thin films prepared by sol–gel process. They showed such films prepared by

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using a non-alkoxide as the main precursor present good oxygen sensing performance at operating temperatures below 470 °C. We previously reported optical and electrochromic properties of dip and spin-coated and time effect on the optical properties of spin-coated CeO_2–TiO_2 thin films [21–23].

The aim of the present work is to examine the optical properties of spin-coated CeO_2–TiO_2 thin films as a function of the coating bath's pH prior to deposition.

2. Experiment

2.1. Film deposition

Mixed CeO_2–TiO_2 thin films were deposited on Corning glass (2947) by sol–gel process using spin-coating technique. The substrate glasses were pre-cleaned with water and liquid laboratory detergent (Non-Ionic Neutral pH Phosphate Free Bio-Degradable) carefully. Then, the substrates were cleaned with de-ionized water in a Bandeline Sonorex RK-100 ultrasonic cleaner, washed with acetone and dried at 80 °C for 30 min. The starting solution was prepared using ceric ammonium nitrate salt dissolved in ethanol and mixed with titanium butoxide, adding a mixture of small amount of distilled water and glacial acetic acid as catalyst depending on the pH of the sol (the pH was measured by a Schott–Geraete GmbH CG840 pH-meter). The solution was mixed with a magnetic stirrer for 24 h. The sol aged for 8 days to obtain a transparent coating. The films were deposited onto substrates using spin-coating method with a spin speed of 2500 rpm. The films were dried at 100 °C for 30 min and the coating procedure was repeated for three times. The process from starting solution to solid films is shown in a flow chart in Fig. 1.
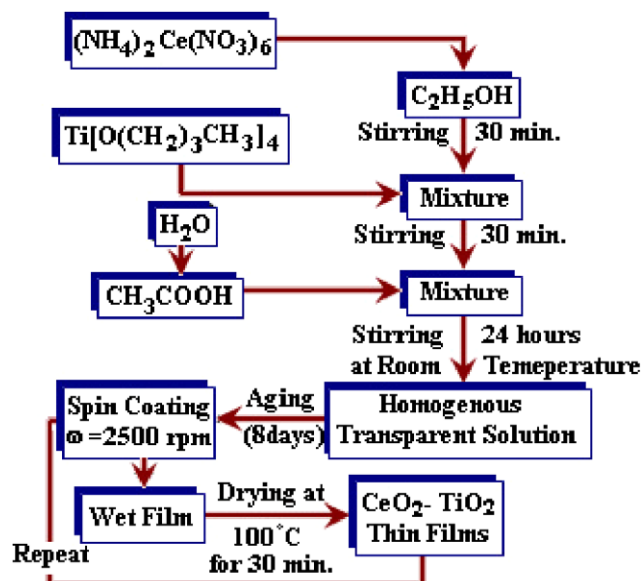
2.2. Sample characterization

The structure of the produced films deposited on glass substrates were characterized by X-ray diffractometer using a PHILIPS PW-1840. The diffractometer is equipped with a Cu rotating anode and a monochromator for sample irradiation and detection of the Cu Kα radiation scattered from the sample surface. The optical transmittance and reflectance of the films were carried out by a spectrophotometer (Aquialla Inst., nkd 7000, UK). The nkd spectrophotometer is a device that is designed to measure transmittance and reflectance of lights incident on a thin film. The refractive index (n), extinction coefficient (k), and thickness (d) of the films were evaluated by the Pro-Optix software incorporated with this device. *The measured data was used for the analysis using the software and fitted* to the normalized Cauchy model. In order to study the fine scale microstructure of CeO_2–TiO_2 thin films atomic force microscopy (AFM) analysis was performed using a scanning probe microscope (SPM-9500, Shimadzu Corp.).

3. Results and discussion

X-ray diffraction studies of CeO_2–TiO_2 thin films coated on glass substrates prepared by different pH are presented in Fig. 2. The XRD studies showed that the film structure is not modified and no peaks of any crystallite phase of CeO_2 and TiO_2 are observed when the pH of sol is changed. The

Fig. 1. Block diagram of the CeO_2–TiO_2 thin films prepared at different pH.
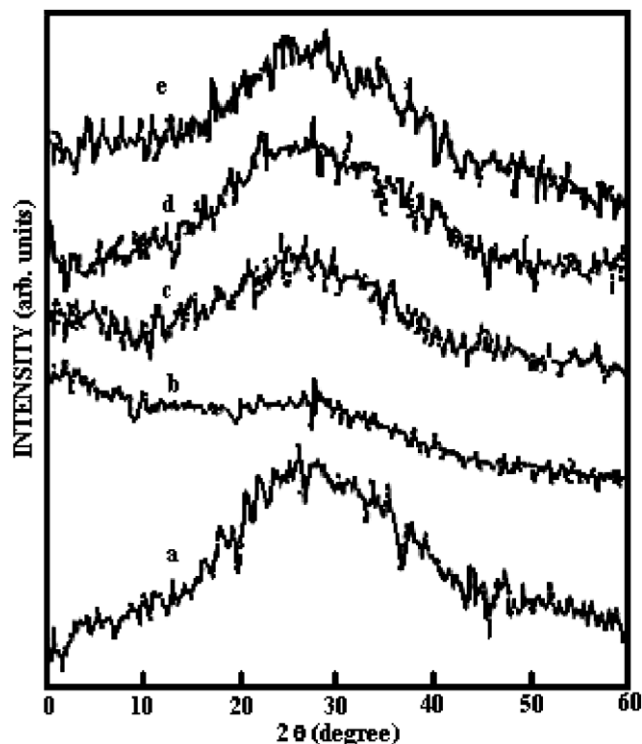
Fig. 2. XRD pattern of sol–gel derived CeO_2–TiO_2 thin films prepared at pH (a) 2.22, (b) 2.35, (c) 2.43, (d) 2.76 and (e) 2.92.

pattern exhibits an amorphous structure of films that seems to be due to the presence of Ce (OR)$_4$ in Ti (OR)$_4$ which inhibits the formation of large groups of Ti–O–Ti bonds and increases the number of defects [12].

Fig. 3 illustrates the AFM images of the CeO$_2$–TiO$_2$ thin films with 3 different pH of the sol. The images show that the structure of the film changes by varying the pH of the sol. Inhomogeneity of thickness of the CeO$_2$–TiO$_2$ thin films was increased from about 10.5–27.8 nm (in RMS) when the pH of the sol increases from 2.35 to 2.92. The film prepared with a pH of 2.35 has more uniform and smoother surface. The surfaces of the films show crack free on explored section (The samples were examined in five different regions with area of $5 \times 5 \, \mu m^2$.).

The transmission-reflection spectra for the spin-coated CeO$_2$–TiO$_2$ thin films deposited on the Corning glass substrates at different pH are shown in Fig. 4. The films exhibit high transmission and low reflection in the visible spectral region. The optical constants and thickness of the CeO$_2$–TiO$_2$ thin films were determined from measured transmittance and reflectance spectra using pro-Optix software installed in the spectrophotometer.

The dispersion of the refractive index for CeO$_2$–TiO$_2$ thin films for different pH is represented in Fig. 5. The inset

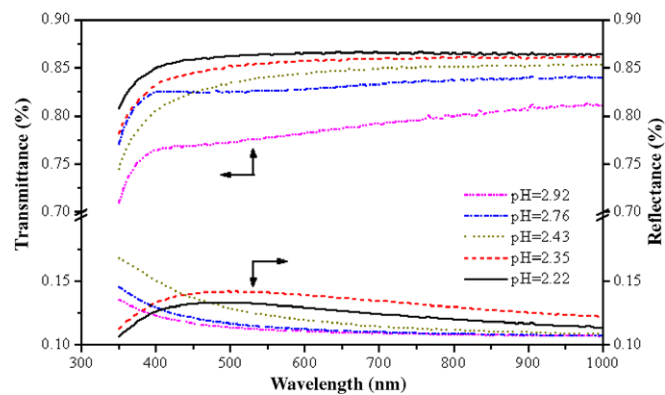
Fig. 4. Transmittance and reflectance curves of the CeO$_2$–TiO$_2$ thin films using sols with different pH.

figure shows the refractive index with respect to the pH. The refractive index at 550 nm increases from 1.49 to 1.61 when the pH rises from 2.22 to 2.92. Fig. 6 shows the spectral behavior of the extinction coefficient with respect to wavelength as a function of pH. The change in the extinction coefficient versus pH is plotted in the inset of the figure. It is shown that the extinction coefficient increases when the pH of sol increases.
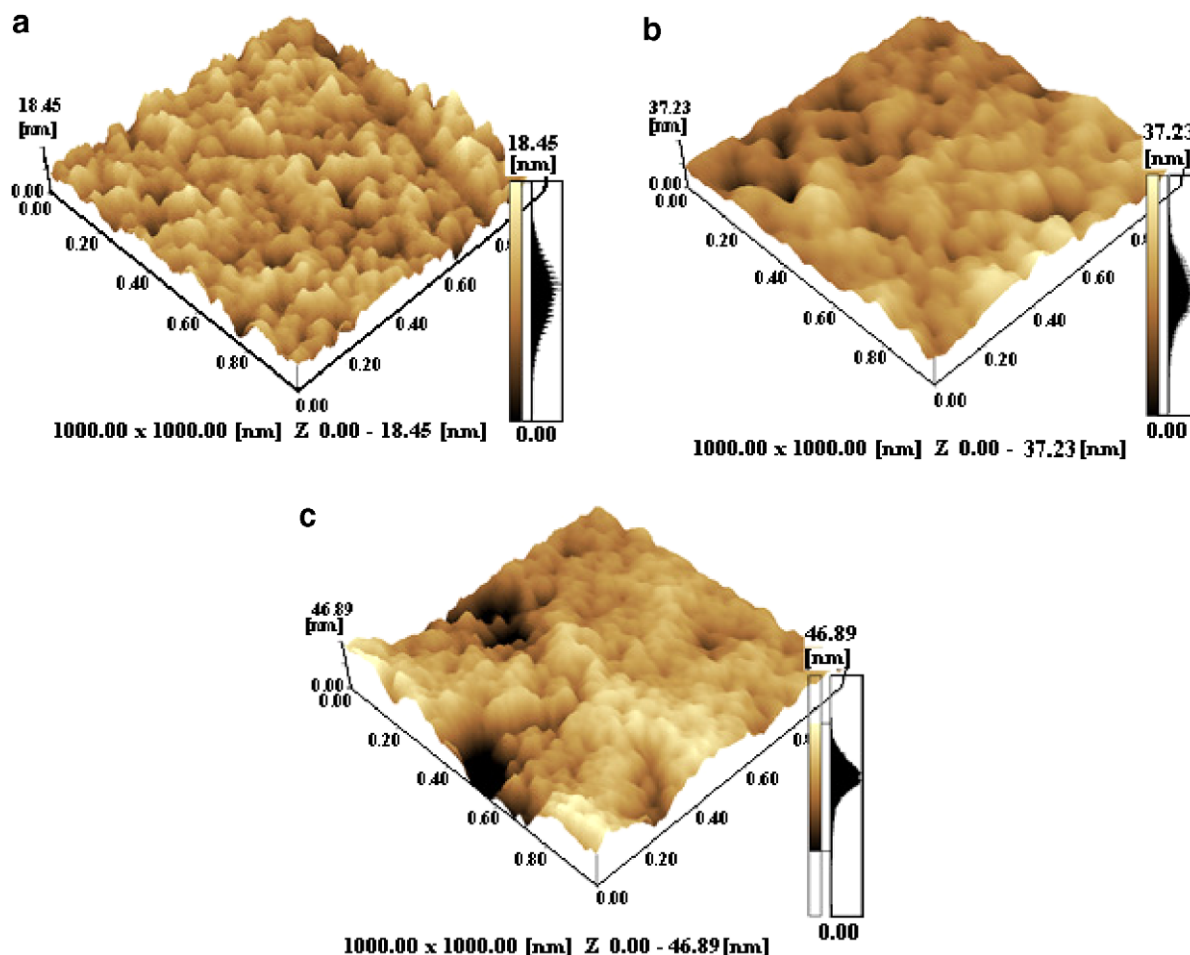

Fig. 3. AFM images of CeO$_2$–TiO$_2$ thin films prepared at pH (a) 2.35, (b) 2.43 and (c) 2.92.
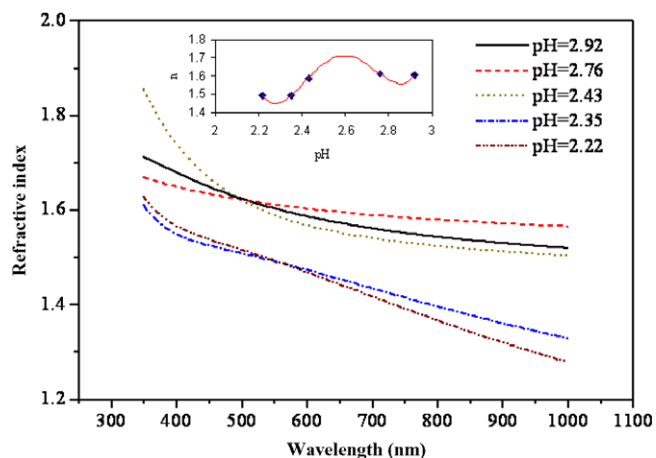
Fig. 5. Changes in refractive index of CeO$_2$–TiO$_2$ thin films with respect to wavelength using sols with different pH. The inset displays the refractive index versus the deposition pH at the wavelength of 550 nm.

Fig. 7. Variation of packing density (p), and film thickness (h) as a function of the deposition pH.

The Bragg and Pippared relationship [24] was used to determine the packing density of the films. The thickness and packing density variation of the films as a function of the pH of the sol is displayed in Fig. 7. The film thickness increases from 46.6 nm to 96.2 nm, and the packing density rises from 0.21 to 0.34 when the pH increases from 2.22 to 2.92.

4. Conclusion

In this work, we studied variations in the optical and structural properties of CeO$_2$–TiO$_2$ thin films resulting from changing the amount of catalyst. It has been shown that varying the pH of the coating bath can change the optical properties of the films. The refractive index, extinction coefficient, and packing density of the films decrease with decreasing the pH of the coating bath. Preparation procedure of the sol *results* particulate film structure.
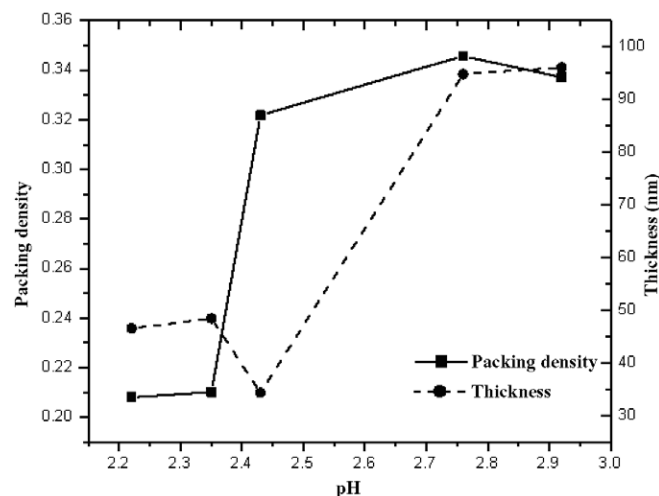
Reduction of the pH results an increase of condensation rate and rise of the porosity of film. Increasing of porosity causes the deposited film to be less packed and as a result, the refractive index of the film to be low [25]. The behavior of extinction coefficient approximately is similar to refractive index. There is an exception for the sample with pH 2.76. It is supposed that the reduction of extinction coefficient at pH 2.76 is due to increasing of randomness of the glass structure [26] that appears as a slope parameter in Urbach relation of absorption coefficient [27]. The porosity of the films can be seen from AFM images related to the optical behavior of the films. The structure of the film is amorphous that can be changed to a crystalline structure if the annealing temperature is made above 500 °C [12].

Fig. 6. Extinction coefficient (k) values of CeO$_2$–TiO$_2$ films with respect to wavelength using sols with various pH. The inset shows Extinction coefficient at the wavelength of 550 nm versus pH.

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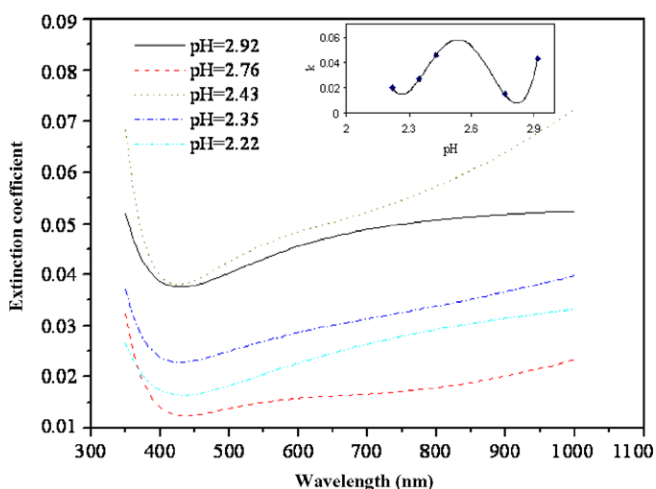[9] A. Makishima, M. Asami, K. Wada, J. Non-Cryst. Solids 100 (1988) 321.

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