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Atomic force microscopy and spectroscopy studies of annealed Ce/Ti/Zr mixed oxide thin films prepared by sol–gel process

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Abstract

Mixed Ce/Ti/Zr oxide thin films with a molar ratio of 0.5:0.25:0.25 were prepared using the sol–gel process, and deposited on glass substrates by the dip coating technique. The effect of heat treatment temperature on surface morphology of the films was examined by atomic force microscopy, AFM. The optical transmittance and reflectance of the films were measured over the spectral range from 350 to 1000 nm. The refractive index and extinction coefficient and thickness of the films were determined as a function of the heat treatment temperature. The refractive index increased from 1.51 to 2.02 at $\lambda = 600$ nm, and the extinction coefficient values increased from 0.006 to 0.094 while the thickness of the films decreased from 81 nm to 45 nm when annealing temperature increased from 100 °C to 500 °C. The results show that the optical properties and surface morphology of the mixed Ce/Ti/Zr oxide thin films were affected by annealing temperature.

Keywords: AFM; nkd Spectroscopy; Sol–gel; Thin films

1. Introduction

Thin films of the metal oxide are very important due to their use in various applications such as optoelectronic [1,2], semiconductor gas sensing devices [3,4], photochromic [5] and electrochromic devices [6,7]. Metal oxide thin films can be prepared by the sol–gel process that offers a low-cost, rapid uniform coating of glass surfaces that renders it potentially interesting for various applications [8,9]. Sol–gel derived thin films that have not been annealed are too impure and too ill defined to be of use in the above-mentioned devices [10]. In this work, we prepared mixed Ce/Ti/Zr oxide thin films with molar ratio 0.5:0.25:0.25 by the sol–gel process using dip coating technique and annealed them at specific temperature between 100 °C and 500 °C. The effects of annealing temperature on the optical and structural properties of the samples studied by an nkd spectrophotometer and atomic force microscope respectively.

2. Experimental

2.1. Thin film preparation

Thin films of mixed Ce/Ti/Zr oxide were deposited using the sol–gel process by dip coating technique, from stabilized solutions prepared as described below. Ceric ammonium nitrate was dissolved in ethanol as main precursor and stirred by magnetic stirrer for 30 min. Then, titanium butoxide, and zirconium propoxide were added into the mixture separately. This mixture was stirred for 30 min. To accelerate hydrolysis and condensation, a small amount of acetic acid and distilled water were added to the mixture. The mixture was stirred for 24 h. A homogenous transparent solution was achieved. This mixed Ce/Ti/Zr oxide solution was aged for eight days at room temperature (16 ± 3 °C) with a humidity of ($50\% \pm 5\%$) to achieve a highly transparent

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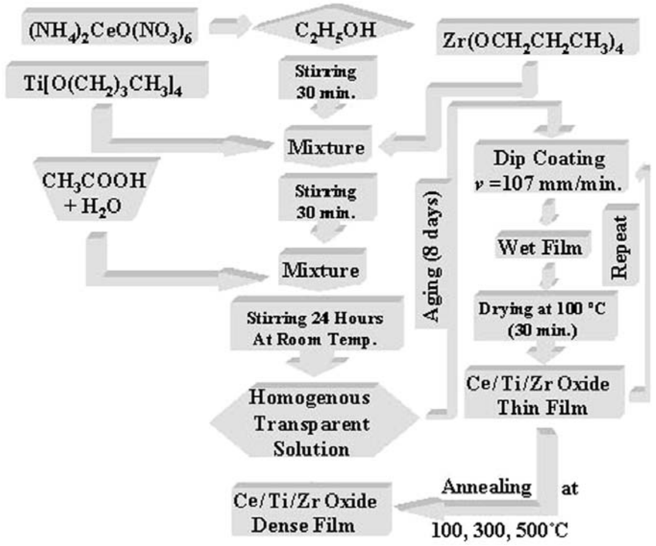

Fig. 1. Flow chart of the mixed Ce/Ti/Zr oxide thin films process.

coating. During aging, the colour of the solution turns from deep red to pale yellow in a few days, indicating a reduction of cerium (IV) by ethanol [11]. Coatings were applied from the sol onto Corning 7059 glass (barium borosilicate) substrates by the dip coating technique at a pull rate of 107 mm/min. The samples were dried for about 1 h at 100 °C after pulling. The process was repeated for three times. The samples annealed in a temperature controllable furnace at 100–500 °C for 1 h at a ramp rate of 60 °C/h. Fig. 1 shows the flow chart of the Ce/Ti/Zr oxide coating process.

2.2. Thin film characterization

Surface structures of the mixed Ce/Ti/Zr oxide thin films were investigated by an atomic force microscope (AFM, Shimadzu). The structure of the produced films deposited on glass substrates were characterized by X-ray diffractometry 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. The optical transmittance and reflectance spectra of the mixed Ce/Ti/Zr oxide thin films were measured using an Aquila 6000 nkd spectrophotometer at an angle of incidence of 30°. The nkd spectrophotometer is a device that is designed to measure transmittance and reflectance of light incident on a thin film. A software (Pro-Optix), incorporated with this device, is used to calculate the refractive index (n), extinction coefficient (k), and thickness (d) of thin films. A Cauchy model [12] was used to fit the experimental data to data generated by software.

3. Results and discussion

The atomic force microscopy (AFM) images of the mixed Ce/Ti/Zr oxide thin films deposited on the Corning glass substrates and annealed at three different temperatures are illustrated in Fig. 2. The surfaces of the films show crack free areas in the explored section (samples were examined in five different regions with area of $5 \times 5\ \mu m^2$). The inhomogeneity in film thickness decreases from about

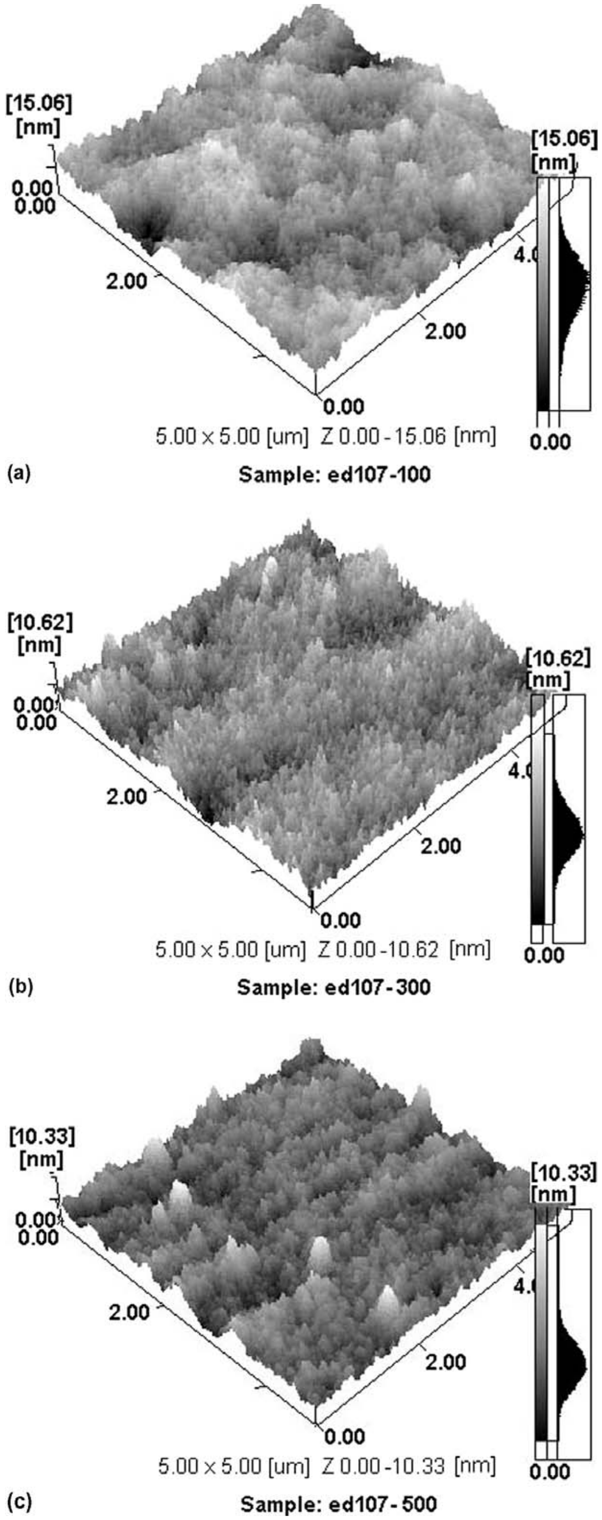

Fig. 2. AFM images of the mixed Ce/Ti/Zr oxide thin films annealed at (a) 100 °C, (b) 300 °C, and (c) 500 °C temperatures.

8.5 nm to 3.6 nm (in RMS) when the annealing temperature increases from 100 °C to 500 °C. The inhomogeneity reduction is slower from 300 °C to 500 °C, showing that the densification of the film reduces after 300 °C. We examined the structural properties of the samples by XRD. The XRD studies showed that film structure is not modified and no peaks of any crystallite phase of CeO_2 and TiO_2 and ZrO_2 are observed when the sample annealed up to 500 °C. The pattern exhibits an amorphous structure of the films.

Fig. 3 represents the wavelength dependence of spectral transmittance and reflectance of the mixed Ce/Ti/Zr oxide thin films deposited by the dip coating technique and annealed at three different temperatures. All films annealed at different temperature are transparent in the visible region. The transparency of the samples decreases with increasing of annealing temperature while their reflectivity increases, indicating a densification of the sol–gel derived films with annealing temperature.

The wavelength dependence of refractive index and extinction coefficient of Ce/Ti/Zr oxide thin films with respect to annealing temperature were calculated from transmittance and reflectance spectra in the range 300–1000 nm. Fig. 4 shows the dispersion of the refractive index (n) of films annealed at 100, 300, and 500 °C. As can be seen, the refractive index of the films increases with increasing annealing temperature, indicating an increase of packing density of the films due to densification and reduction of porosity. The same behaviour was observed for the extinction coefficient of the films with increasing annealing temperature. The plot of extinction coefficient of the films versus wavelength with respect to annealing temperature is illustrated in Fig. 5. The measured spectral transmit-

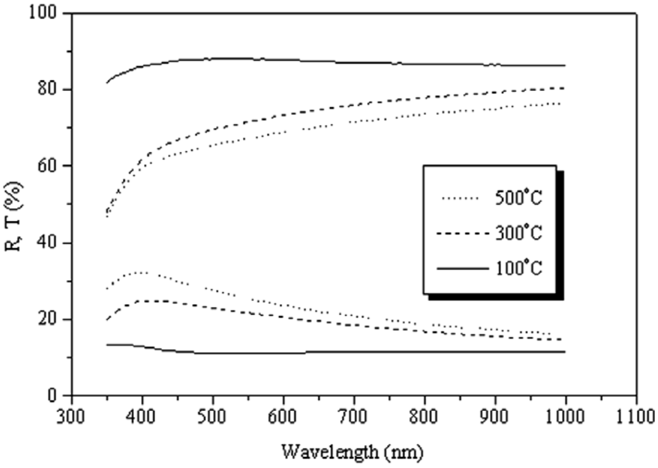

Fig. 3. Transmittance and reflectance against wavelength of the mixed Ce/Ti/Zr oxide thin films prepared by sol–gel process and annealed at (a) 100 °C, (b) 300 °C, and (c) 500 °C temperatures.

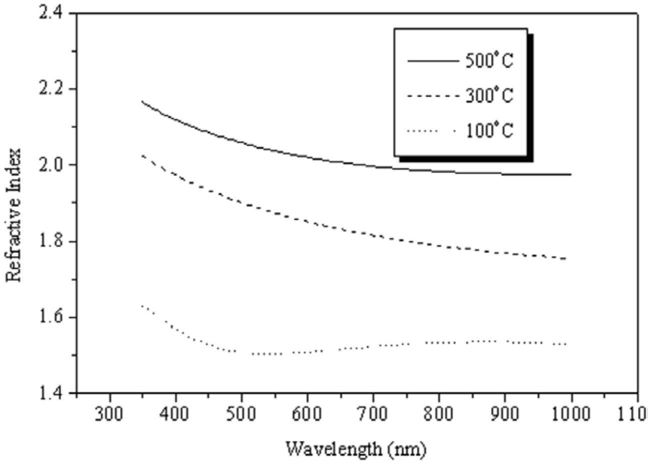

Fig. 4. Refractive index of the mixed Ce/Ti/Zr oxide thin films prepared by sol–gel process and annealed at 100 °C, 300 °C, and 500 °C temperatures.

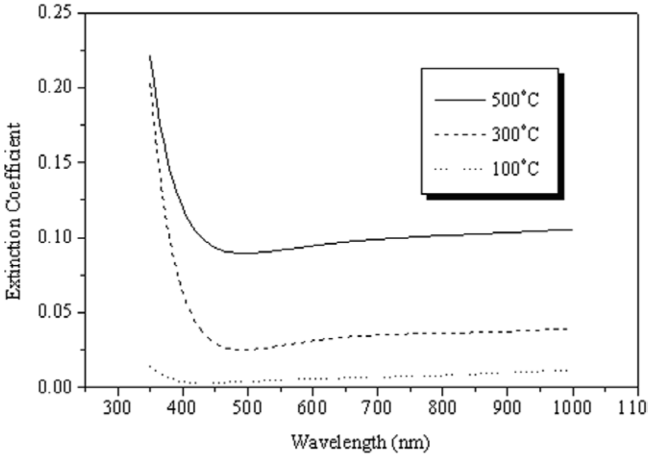

Fig. 5. Wavelength dependence of Extinction coefficient for the mixed Ce/Ti/Zr oxide thin films prepared by sol–gel process and annealed at 100 °C, 300 °C, and 500 °C temperatures.

Table 1
The measured spectral transmittance, reflectance, roughness, and calculated refractive index, extinction coefficient and thickness of Ce/Ti/Zr oxide thin films annealed at different temperature

Annealing temperature (°C)	Transmittance (%)	Reflectance (%)	Refractive index	Extinction coefficient	Thickness (nm)	Roughness (rms) (nm)
100	88	11	1.510	0.006	80.8	8.5
300	69	21	1.851	0.031	58.8	4.1
500	73	24	2.020	0.094	44.5	3.6

The optical constants determined at $\lambda = 600$ nm.

tance, reflectance, thickness inhomogeneity, and calculated refractive index, extinction coefficient and thickness of sol–gel derived Ce/Ti/Zr oxide thin films annealed at 100, 300, and 500 °C are listed in Table 1.

4. Conclusion

Mixed Ce/Ti/Zr oxide thin films were prepared using sol–gel process successfully. The samples were annealed at 100, 300, and 500 °C annealing temperatures. Atomic force microscopy analyses show that the surfaces of the films have been changed with varying annealing temperature. Optical measurements and calculations show that the refractive index and extinction coefficient of the films increases with increasing annealing temperature while the thickness of the films decreases. The results showed that annealing temperature increased the density the sol–gel derived Ce/Ti/Zr oxide thin films resulting in higher refractive index, extinction coefficient and lower thickness as expected. Increasing of the optical constants is due to an increase of the packing density that is associated with a reduction of porosity in the film. The results show that the production of sol–gel derived Ce/Ti/Zr oxide thin films with a variety of optical and structural properties are possible.

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