

Comparison of Five-Layered ZrO_2 and Single-Layered Ce, Eu, and Dy-Doped ZrO_2 Thin Films Prepared by Sol-Gel Spin Coating Method

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In order to investigate the influence of the number of layers on the properties of ZrO_2 thin films, we prepared one pure ZrO_2 film sample with five layers and Ce, Eu, and Dy-doped ZrO_2 samples with single layer, by spin-coating sol gel-method. The crystal structures of thin films were determined using X-ray diffraction, morphology of the samples was analyzed by scanning electron microscopy, and the optical properties of the samples were determined by ultraviolet/visible absorbance measurements. The results of these measurements have shown that the concentration of the dopants and the thickness of thin film layers play a vital role in the physical, chemical, and optical properties of the pure and doped ZrO_2 thin films.

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1. Introduction

Zirconium oxide (ZrO_2) is useful for technological applications due to its high refractive index, high transparency in the visible and near-infrared regions, high dielectric constant, high-energy band gap, high density, high hardness, high electrical conductivity, strong wear resistance, high fracture toughness, low thermal conductivity and extreme chemical inertness [1–7]. Zirconium oxide has found use in many diverse applications, including catalysis, surface supports, laser systems, gate dielectrics, optical and electronic devices, magnetic recording disks, and biomedical and prosthetic coatings [8–11]. Doping of ZrO_2 with rare earth metal oxides (Ce, Dy and Eu) can be used to improve its optical and dielectric properties [5, 12].

A thin film is a layer of material, with thickness ranging from a nanometer to a few micrometers, on a substrate. Many oxide materials have been used extensively in the form of the thin films [2]. In thin film fabrication technology, many different types of methods are used, such as electron beam evaporation [13], metal-organic chemical vapor deposition [2], atomic layer deposition [14], RF magnetron sputtering [15], thermionic vacuum arc deposition [16], pulsed laser deposition [3] and sol-gel method [17–19].

The sol-gel technique is preferred for many applications because it is a room temperature process of low cost, with inexpensive equipment [20], good homogeneity, low processing temperature, large area of coating and good

optical properties [21, 22]. Sol-gel technique has got several methods such as spin-coating, dip-coating, spray coating, flow coating, laminar coating, roll coating and printing [23].

In this work, we first, produced 1, 2, 3, 4 and 5 ZrO_2 thin films layers on glass substrate sequentially, on top of each other. Then in a similar way three different, 1 mole %, Ce, Dy and Eu-doped ZrO_2 thin films, consisting of one layer, were prepared by spin-coating sol-gel technique on glass substrates. Crystal structure, surface morphology, thermal properties and optical properties of ZrO_2 thin films were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet/visible (UV/VIS) absorption spectrometry, respectively.

2. Experimental

For the preparation of the solutions of the pure and Eu, Ce and Dy doped ZrO_2 thin films, we used Zr iso-propoxide $\text{Zr}[\text{OCH}(\text{CH}_3)_2]_3$ (99.9% purity, $M_w = 383.68$ g/mol) and $\text{Dy}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Aldrich, 99.9%, $M_w = 348.51$ g/mol (anhydrous basis)), $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Aldrich 99.9%, $M_w = 428.06$ g/mol), and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (>99% purity, $M_w = 434.22$ g/mol), as starting reagents and the absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Sigma-Aldrich, 99.8%, $M_w = 46.07$ g/mol).

The preparation of the solutions for deposition of thin film samples has been carried out as follows. Firstly, we poured 80 ml of propanol and 10 ml of ethanol in a beaker and stirred this mixture for half of an hour. During mixing, 20 drops of acetic acid were slowly dropped into solution. Then we added 20 ml of Zr iso-propoxide into

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the solution and mixed it for 1 h. During this time, we added 150 ml of propanol into this solution and we continued mixing it for 2 h. This final solution was transferred equally into four separate beakers.

One of these solutions was used for the fabrication of the pure ZrO_2 thin films. The other three solutions were used to obtain 1 mole % Eu, Dy and Ce doped- ZrO_2 solutions. To obtain these solutions, we dissolved 0.025 g of Eu nitrate, 0.02 g of Dy nitrate, and 0.025 g of Ce nitrate into the three separate beakers, containing 2 ml of ethanol, and poured each of these solutions into the ZrO_2 solutions which were prepared in advance, as mentioned above. Finally, these four solutions were mixed for 1 h until they became homogeneous.

The layered ZrO_2 films were prepared by spin-coating on the glass substrates, using the prepared sol-gel solution. To do this, firstly the sol was dripped on the substrate and spun at a rate of 2000 rpm for 30 s using a G3 Spin Coater (SCS Spin Coating Systems). Thus the first layer was formed on the substrate and then it was dried at 100 °C in a furnace. After this process, the second layer was formed on top of the first layer and dried, as was mentioned above. The same process was applied to form five layers. After completing these processes, the sample was annealed at 500 °C.

Single-layered ZrO_2 thin films, doped with 1 mole % Eu, Ce and Dy were fabricated on glass substrates, using the same process, applied to fabricate only one layer. Finally, the characterization of these samples was conducted. The optical properties of the films were studied using Perkin Elmer lambda 20 UV spectrometer. The microstructural features of the samples were determined using SEM (LEO 1430 VP). X-ray diffractometer (X Pro Alpha) was used in order to determine the crystal structure of the thin films. Thermal analysis of the samples was conducted with a TG-DTA (Netzsch STA449F3) at a heating rate of 20 K/min, under air atmosphere in aluminum pans, at temperatures ranging from ambient 25 °C to 550 °C.

3. Results and discussion

The thermal behavior of the prepared samples has been first investigated by TG-DTA. The samples were tested under a heating rate of 10 °C/min in air atmosphere. DTA/TG diagrams of pure ZrO_2 thin film with five layers, and 1 mole% Dy, Ce, Eu-doped ZrO_2 thin films with a single layer, prepared at 500 °C, are given in Fig. 1a–d.

Differential thermal analysis (DTA) of pure ZrO_2 thin film is presented in Fig. 1a. It is observed that the crystallization of ZrO_2 starts at the temperature of 400 °C.

The thermogravimetric analysis (TGA) indicates that the weight loss is observed for every sample. Weight loss in the range between 50 and 400 °C is ascribed to the removal of absorbed water molecules from the samples. The process has resulted in the synthesis of pure ZrO_2 with the total weight loss of 16.89 mg (29.44%) in the temperature range between 50 °C and 500 °C (Fig. 1a).

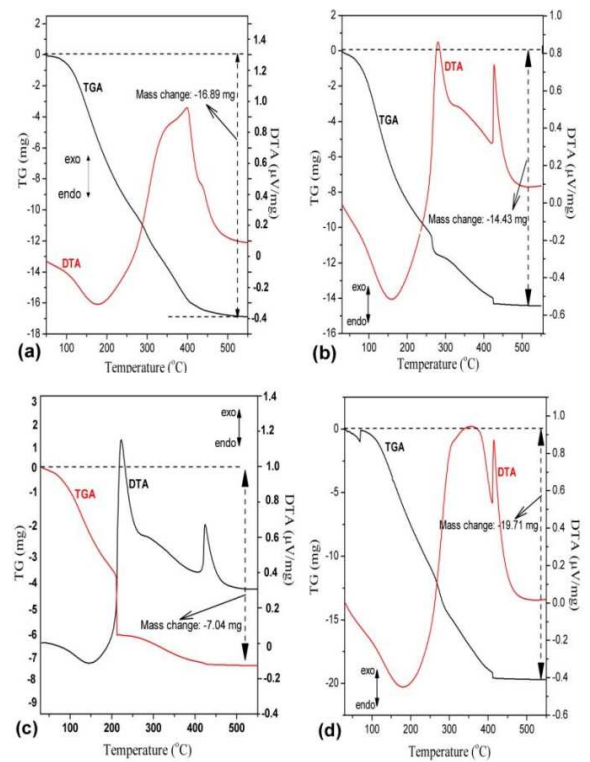


Fig. 1. DTA/TG diagrams of (a) pure ZrO_2 thin film with five layers, and ZrO_2 thin films with single layer, doped with 1 mole % of (b) Dy, (c) Ce and (d) Eu, prepared at 500 °C.

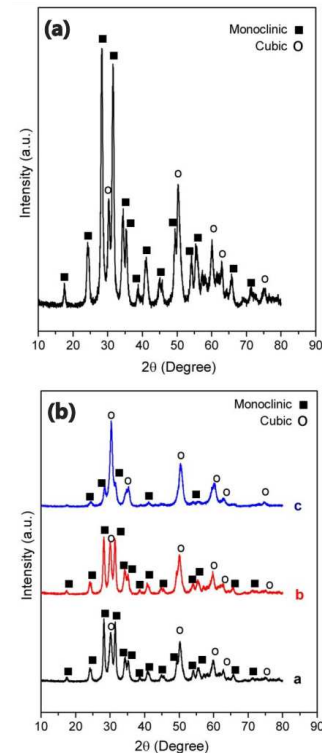


Fig. 2. (a) XRD patterns of pure ZrO_2 thin film, heat treated at 500 °C, and (b) XRD patterns of ZrO_2 thin films, doped with 1 mole % of Dy (curve a), Ce (curve b), and Eu (curve c), heat treated at 500 °C.

Total weight losses of ZrO_2 doped with 1 mole % Dy (Fig. 1b), Ce (Fig. 1c) and Eu (Fig. 1d) were 14.43 mg (34.12%), 7.04 mg (32.79%), and 19.71 mg (30.69%), respectively. Weight loss terminates at 300 °C (Fig. 1b), where Dy nitrate was completely converted into Dy_2O_3 , after a gradual loss of crystalline water. The chemical conversion reactions of decomposition of Ce and Dy nitrate into CeO_2 and Eu_2O_3 , have been realized at 250 °C and 350 °C, respectively, (Fig. 1c and d).

Figure 1a also shows that the DTA curve for pure ZrO_2 indicates oxidation temperature of 400 °C. It is observed that 1 mole % Dy, Ce and Eu-doped ZrO_2 materials have higher oxidation temperatures of 430 °C, 430 °C and 420 °C, respectively. Similar results have been obtained for similarly doped ZrO_2 [24]. There is no significant

weight loss at and above 450 °C.

XRD patterns of the pure and Ce, Eu, and Dy-doped ZrO_2 samples are given in Fig. 2. The intensity of diffraction peaks, corresponding to monoclinic phase, is relatively higher than the intensity of XRD peaks corresponding to cubic phase. It is seen that there are no substantial changes between the pure and Ce and Dy-doped ZrO_2 thin films. However, XRD pattern of Eu-doped ZrO_2 differs from those of pure and Ce, Dy-doped ZrO_2 . Here there are more cubic than monoclinic ZrO_2 peaks.

The SEM imaging was performed to study the surface morphology. SEM images of pure ZrO_2 thin films (1st–5th layers) and of single layer of 1 mole % Ce, Dy, Eu-doped ZrO_2 thin films are given in Fig. 3a and b, respectively.

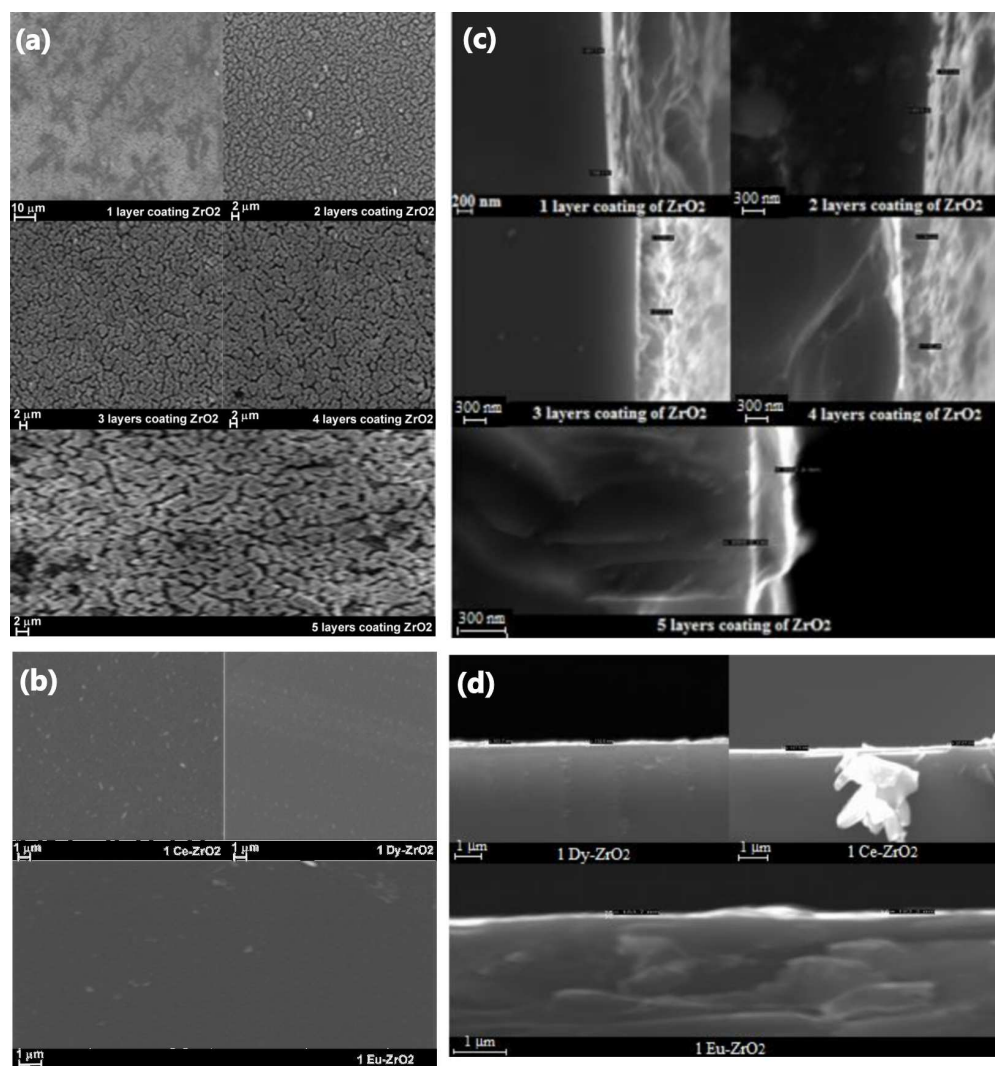


Fig. 3. (a) SEM images of 1st to 5th layers of pure ZrO_2 thin films prepared by spin-coating methods. (b) Single layered 1 mole % Ce, Dy and Eu-doped ZrO_2 thin films. (c) Layer thickness of 1 to 5 layers of pure ZrO_2 thin films, prepared by spin-coating method. (d) Layer thickness of 1 mole % Ce, Dy and Eu-doped ZrO_2 thin films prepared by spin-coating method.

Figure 3c shows the cross section micrographs of the pure ZrO_2 thin films prepared by spin-coating method. It is seen that thickness of layer increases with the number

of coating cycles. The average film thicknesses of pure ZrO_2 (from 1 to 5 cycles) are 476, 573, 896, 910 and 1346 nm, respectively. Figure 3d gives the cross section

micrographs of the single layer of 1 mole % Ce, Dy, Eu-doped ZrO₂ thin films. The average film thickness of Ce, Dy, Eu-doped ZrO₂ thin films are 114, 149 and 183 nm, respectively. It is seen that thickness of film changes with the doping element.

As seen from Fig. 3a and b, very qualitative coating has been achieved by spin-coating sol-gel method. The doped ZrO₂ film samples have shown smooth and uniform surfaces without any cracks. No significant changes in the surface morphology of the thin films doped with 1 mole % of Ce, Dy, Eu were detected.

The absorption spectra of the ZrO₂ films were measured using an UV-Vis spectrometer, by scanning from 190 to 1100 nm. Figure 4a and b shows the absorbance spectra of 1–5 layers of pure ZrO₂ thin film and of single layered 1 mole % Ce, Dy and Eu-doped ZrO₂ thin films, respectively. In the range of 190–1100 nm the pure ZrO₂ thin film shows a larger absorbance than the doped thin films. A drastic change in the absorbance was observed.

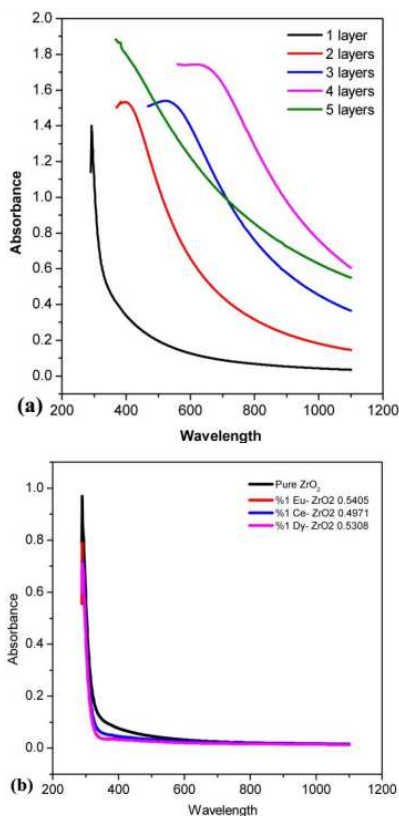


Fig. 4. Optical absorbance spectra of (a) 1–5 layers of pure ZrO₂ thin films and (b) of single layered 1 mole % Ce, Dy and Eu-doped ZrO₂ thin films.

4. Conclusions

Five-layered pure and single layered Ce, Eu, and Dy-doped ZrO₂ thin films were successfully synthesized on glass substrates by sol-gel spin-coating method. The results obtained from the characterization measurements of the samples are as follows;

XRD measurements have shown that there are no substantial changes between the pure and Ce and Dy-doped ZrO₂ thin films. However, the XRD patterns of Eu-doped ZrO₂ differ from those of pure and Ce and Dy-doped ZrO₂. There are more cubic ZrO₂ peaks than monoclinic. It has been observed that very qualitative coatings could be achieved by spin-coating sol-gel method with smooth and uniform surfaces, and without any cracks after the fabrication of the Dy, Ce, and Eu-doped ZrO₂ film samples. Finally, optical absorbance measurements of the samples have shown that the optical properties of thin films are influenced by the doping elements.

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