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Y_2O_3 stabilized ZrO_2 thin films deposited by electron-beam evaporation: Optical properties, structure and residual stresses

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ABSTRACT

This paper describes the preparation and the characterization of Y_2O_3 stabilized ZrO_2 thin films produced by electric-beam evaporation method. The optical properties, microstructure, surface morphology and the residual stress of the deposited films were investigated by optical spectroscopy, X-ray diffraction (XRD), scanning probe microscope and optical interferometer. It is shown that the optical transmission spectra of all the YSZ thin films are similar with those of ZrO_2 thin film, possessing high transparency in the visible and near-infrared regions. The refractive index of the samples decreases with increasing of Y_2O_3 content. The crystalline structure of pure ZrO_2 films is a mixture of tetragonal phase and monoclinic phase, however, Y_2O_3 stabilized ZrO_2 thin films only exhibit the cubic phase independently of how much the added Y_2O_3 content is. The surface morphology spectrum indicates that all thin films present a crystalline columnar texture with columnar grains perpendicular to the substrate and with a predominantly open microporosity. The residual stress of films transforms tensile from compressive with the increasing of Y_2O_3 molar content, which corresponds to the evolutions of the structure and packing densities.

1. Introduction

Y_2O_3 stabilized ZrO_2 (YSZ) thin films exhibit many remarkable properties, which confer on them a role of great interest both in theoretical studies and in practical applications. Their excellent stability and high oxygen ionic conductivity over wide range of temperatures, oxygen partial pressure, low thermal conductivity and good erosion resistance offer the possibility of practical applications in solid oxide fuel cells [1,2], thermal barrier coatings [3–5], etc. YSZ films have also a wider range of potential applications in optical coatings such as high reflectivity mirrors and multiple layer systems for optical filters [6–8] due to their excellent properties such as high refractive index and broad region of low absorption.

Many techniques, including electron-beam evaporation [9], sputtering [10] and various chemical vapour deposition techniques [11,12] can be employed to deposit YSZ coatings. Among them, electron-beam evaporation method is a very attractive process for the production of thin and thick coatings on large and complex shaped substrates due to the low cost of equipment and a high deposition rate. In previous work, our research team has studied the influence of different Y_2O_3 content on the structure, morphological characterization and laser induced damage threshold of YSZ thin films [13]. In this paper, which represents a continuation of that earlier work, four kinds of YSZ films were deposited by electron-beam evaporation method. The effect of various Y_2O_3 contents on the optical properties and microstructure is described, the surface morphology and residual stress are revealed too.

2. Experimental

YSZ thin films were deposited on BK7 glass substrates (borosilicate crown glass supplied by Shanghai Xinhu Glass Factory, China) by electron-beam evaporation in model ZZS-550 vacuum coating system (made by Beijing Beiyi Vacuum Technology Co. Ltd., China). The glass substrates had a 30 mm diameter and their thickness was 3 mm. Before deposition they were cleaned ultrasonically in alcoholic solution. The base vacuum of all depositions was 2.3×10^{-3} Pa, ultrahighpurity oxygen with purity of 99.99% was used to backfill the chamber in deposition processes, and the pressures were kept 1.0×10^{-2} Pa. All deposition temperatures were performed at 300 °C and the deposition rates kept at 0.4 nm/s. The film thickness was controlled by the single-wavelength turning point method with a wavelength of 550 nm and the optical

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thickness was $8\lambda/4$ ($\lambda = 550$ nm). The starting material was grey sintered aggregate of mixed ZrO_2 (99.99%) and Y_2O_3 (99.99%) powder. The ratio of added Y_2O_3 to the ZrO_2 was 0, 3, 7, and 12 mol%, respectively. The granular starting materials were premelted for about 40 min to make the surface even and remove any contamination on their surface before deposition.

The optical measurements of transmission spectra at normal incidence were carried out by Lambda900 spectrophotometer (Perkin Elmer Company) in the wavelength range 300–1200 nm. The measurement accuracy of the equipment was ±0.08%. The refractive index and physical thickness of the films were calculated from the transmission spectra by envelope method. Two different XRD measurements were made for starting evaporation materials and films. Phase composition of the starting materials was characterized by conventional X-ray diffraction (XRD) (Rigaku D/max-2550 system with standard Bragg–Brentano focusing geometry), and the microstructure of the films was characterized by grazing angle X-ray diffraction with Cu Kα_1 radiation ($\lambda = 0.154056$ nm) and 2θ angle was in the range of 20–80° with step size of 0.02°. The average grain size of thin films could be estimated by Scherrer formula, using the full width at half maximum (FWHM) value of the XRD peaks as follows [14]:

$$D = 0.9\lambda/B\cos\theta \quad (1)$$

where D, λ, θ, and B are the mean grain size, X-ray wavelength of 0.154 nm, Bragg diffraction angle, and FWHM of the diffraction peak, respectively. Surface morphology of samples was detected by Veeco Dimension 3100 scanning probe microscope.

3. Experimental results and discussions

3.1. Optical properties

YSZ films have been prepared from several starting materials as reported above and below the same conditions. The film thickness was about 550 nm. The optical transmission spectra of the films are shown in Fig. 1. It is shown that the optical transmission spectra of all the YSZ thin films are similar with those of ZrO_2 thin film, possessing high transparency in the visible and near-infrared regions. The peak transmittance values are even above those of the blank substrate which indicates that the films are optically inhomogeneous. If the films are homogenous, the peak transmittance value corresponds to the transmittance of the substrate. This type of inhomogeneity is typical for many metal–oxide dielectric thin films, and electron-beam-deposited ZrO_2 films are known to be inhomogeneous as well. This results from the fact that the evaporated zirconia films have a columnar structure, with column diameters changing with distance from the substrate side of the film. The most successful model that explained the origin of the optical inhomogeneity in thin films was formulated by Harris et al. [18]. They proposed that inhomogeneity of refractive index results from a density gradient in the growth direction of the thin film. Depending on the deposition conditions, the refractive index of the films at the substrate interface can be either higher or lower than at the film surface.

Fig. 2 shows the refractive index (550 nm) of the films vs. different Y_2O_3 molar contents. It can be found that the refractive index depends strongly on the amount of the stabilizer in the binary system and presents a monotonic decrease. The refractive index of the films varies almost continuously from 1.94 to 1.86 with the increasing of Y_2O_3 content. This makes it possible to use these films in optical applications with the requirement of different refractive indexes. Similar results have already been observed by Boulouz et al. [15] for Y_2O_3 and CaO stabilized zirconia and by Garcia et al. [17] for yttria content in the range from 3 to 12 mol%.

The decrease of the refractive index of the films is the effect of film packing density. The film packing density was determined using the expression of Bragg and Pippard model [18].

$$P = \frac{n_f^2 - 1}{n_f^2 + 2}\frac{n_b^2 + 2}{n_b^2 - 1} \quad (2)$$

where n_f is the refractive index of the film at the given wavelength and n_b is the bulk value of refractive index. Here, used refractive index is the effective index of the mixture and is given by the Lorentz–Lorenz [19] model. It was estimated that the effective indices of four kinds of YSZ thin films are 2.21, 2.20, 2.18, and 2.16, respectively ($\lambda = 550$ nm). So, the film packing density as a function of Y_2O_3 content is shown in Fig. 2. Evaporated YSZ films have a relatively low packing density and the value decreases as the Y_2O_3 content increases. On the one hand, this is because not only the mass of Y^{3+} ions is lighter than that of Zr^{4+} ions but also the radius of Y^{3+} is bigger than that of Zr^{4+}. On the other hand, this functional dependence is expected since as the Y_2O_3 content is increased there is an increase in volume contribution of vacancies generated because of the different valence states of Zr^{4+} and Y^{3+}. Films with lower densities have lower refractive indexes. So the refractive index of the films decreases with the increase of Y_2O_3 content.

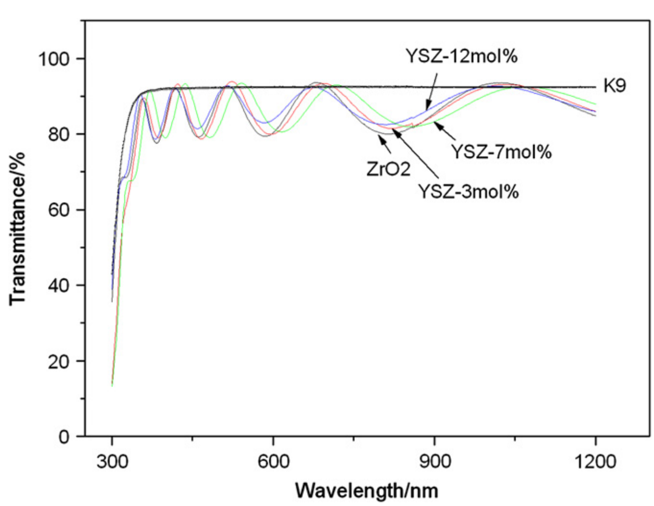

Fig. 1. Transmission spectra of YSZ thin films with different Y_2O_3 contents.

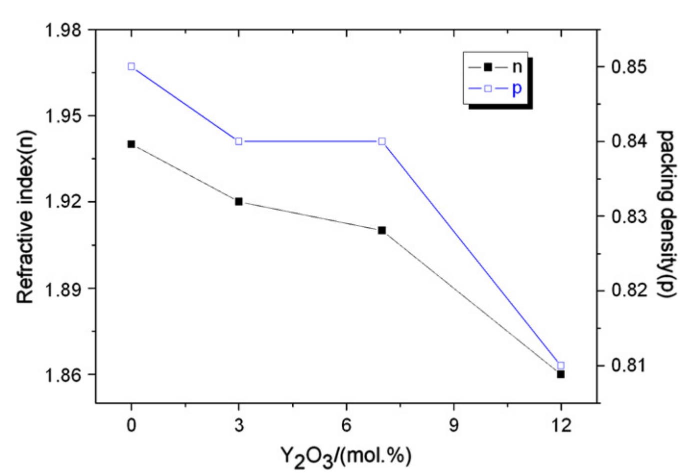

Fig. 2. Refractive index and packing density vs. Y_2O_3 molar percent of YSZ thin films.