Influences of Y_2O_3 dopant content on residual stress, structure, and optical properties of ZrO_2 thin films

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Four kinds of Y_2O_3 stabilized ZrO_2 (YSZ) thin films with different Y_2O_3 contents (from 0 to 12 mol%) are deposited on BK7 glass substrates by electron-beam evaporation method. The effects of different Y_2O_3 dopant contents on residual stress, structure, and optical properties of ZrO_2 thin films are investigated. The results show that residual stress in YSZ thin films varies from tensile to compressive with the increase of Y_2O_3 molar content. The addition of Y_2O_3 is beneficial to the crystallization of YSZ thin film and transformation from amorphous to high temperature phase, and the refractive index decreases with the increase of Y_2O_3 molar content. Moreover, the variations of residual stress and the shifts of refractive index correspond to the evolution of structures induced by the addition of Y_2O_3.

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Zirconium dioxide (ZrO_2) is useful for optical devices because of its desirable properties such as high refractive index, high transparency in the visible and near-infrared region, and high damage threshold value of repetitive pulsed laser[1,2]. As a pure material, it exists in the monoclinic, tetragonal, and cubic structures. Phase transformations between ZrO_2 polymorphs are accompanied by significant volume change, which causes the variation of residual stress and deteriorates the mechanical performances. One of the effective ways to obtain stable single phase is to add a convenient amount of other oxides, such as CaO, Y_2O_3, etc.[3,4]. Especially, Y_2O_3 is the most frequently used material as a stabilizer.

Y_2O_3 stabilized ZrO_2 (YSZ) thin film has been stabilized in high temperature phases (tetragonal and cubic phase) with the phase transition restrained, which exhibits excellent characteristics such as superior optical properties, chemical durability, corrosion resistance, and low thermal conductivity. Previous reports showed that it was extensively used as high reflectivity mirrors, thermal barrier coatings, and multi-layer systems for optical filters[4–7]. The objective of this letter is to make a comparative study of the effects of different Y_2O_3 contents (0, 3, 7, 12 mol%) on residual stress, structure, and optical properties of ZrO_2 matrix films. Moreover, the relationship between the structure and residual stress of the films is investigated.

All the samples were deposited on BK7 glass substrates ($\Phi 30 \times 3$ (mm)) by electron beam evaporation in ZZS-550 vacuum coating system. The substrates were cleaned ultrasonically in alcoholic solution. The base vacuum of all depositions was 2.0×10^{-3} Pa, meanwhile the O_2 deposition pressure was 1.0×10^{-2} Pa. The deposition temperature was approximately 200 °C and the deposition rate was 0.8 nm/s. The optical thickness of all films was 8 quarter-wavelength optical thicknesses under optical control at a wavelength of 550 nm. Four different Y_2O_3 content mixtures were used as evaporation materials. More details of the inhouse made evaporation materials were presented in Ref. [8]. The transmission spectra were measured by Lambda900 spectrophotometer (Perkin Elmer Company). The measurement accuracy of the equipment was ±0.08%. The refractive index and thickness of the films were calculated from the transmission spectra. An energy dispersive spectroscope (EDS) was used for chemical composition measurements in the films, to testify whether the Y_2O_3 to ZrO_2 ratio of coatings with different Y_2O_3 molar contents were in agreement with that of the starting coating materials. The microstructures of four kinds of YSZ films were characterized by X-ray diffraction (XRD) using a Dmax-2500 system, with Cu Kα radiation ($\lambda = 0.154056$ nm), and the 2θ angle was in the range of $20° - 80°$ with a step size of 0.02°. The substrate radius of curvature was measured by a ZYGO interferometer. The residual stress σ in the film is then given by Stoney's equation[9]:

$$\sigma = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_f} \left(\frac{1}{R_1} - \frac{1}{R_0} \right), \tag{1}$$

where $\frac{E_s}{1-\nu_s} = E'_s$ (102 GPa) is the biaxial modulus of the substrate, E_s and ν_s are Young's modulus and Poisson ratio of the substrate; R_0 and R_1 are the curvature radii of the substrate before and after deposition; t_s and t_f are the thicknesses of the substrate and the film, respectively.

The Y_2O_3 concentration of the films was analyzed by EDS. Figure 1 shows the EDS spectra of the four kinds of YSZ thin films. According to the EDS spectra, the Y_2O_3 molar contents of four kinds of YSZ thin films are 0, 2.7, 6.8, and 11.8 mol%, respectively. Within the precision of EDS measurements, the Y_2O_3 to ZrO_2 ratios of four kinds of YSZ thin films present rather good chemical homogeneity, which is in good agreement with the starting coating materials. These results prove that starting coating materials are stable and do not have loss in the

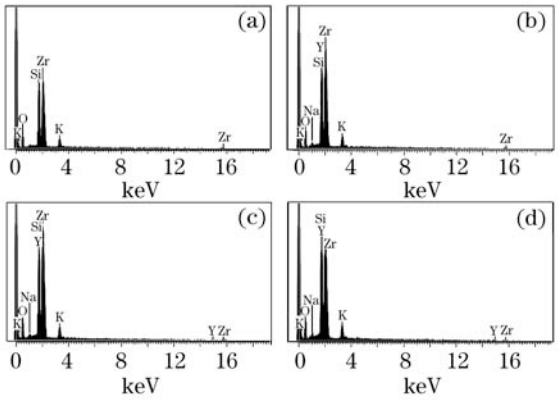

Fig. 1. EDS spectra of the YSZ thin films with (a) 0 mol%, (b) 3 mol%, (c) 7 mol%, and (d) 12 mol% Y_2O_3.

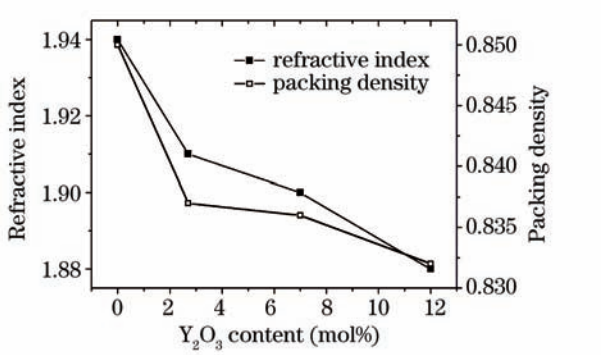

Fig. 2. Refractive index at 550 nm and packing density versus the Y_2O_3 concent.

thin film preparation process.

Figure 2 shows the variation of refractive index at 550 nm of the films with different Y_2O_3 concents, according to the envelope method developed by Manifacier *et al.*[10]. It is shown that as the concentration of the stabilizer increases, the refractive index of films decreases gradually. Similar results were observed by Boulouz *et al.* for Y_2O_3 and CaO stabilized zirconia[11]. This may be attributed to the variation of the packing density (as shown in Fig. 2). The refractive index data are indicative of the film packing density. The relation between refractive index n_f and packing density p is determined using the expression of Bragg and Pippard model[12]:

$$p = \frac{n_f^2 - 1}{n_f^2 + 2} \frac{n_b^2 + 2}{n_b^2 - 1}, \tag{2}$$

where n_b is the bulk value of refractive index at the given wavelength. For the Y_2O_3 stabilized ZrO_2, the effective indices of the mixture, n_b, calculated from the Lorentz-Lorenz expression[13], are 2.21, 2.20, 2.18, 2.16 ($\lambda = 550$ nm), respectively. Therefore, the packing density decreases with the increase of Y_2O_3 content and the value changes almost continuously from 0.85 to 0.832.

The values of residual stress of YSZ thin films with different Y_2O_3 molar contents are given in Fig. 3. We can see that the residual stress in the pure ZrO_2 thin films (without Y_2O_3) deposited at 200 °C is tensile with a value of 115 MPa; with the increase of Y_2O_3 molar content, the residual stress decreases. When the Y_2O_3 molar content increases to 7 mol%, the residual stress becomes

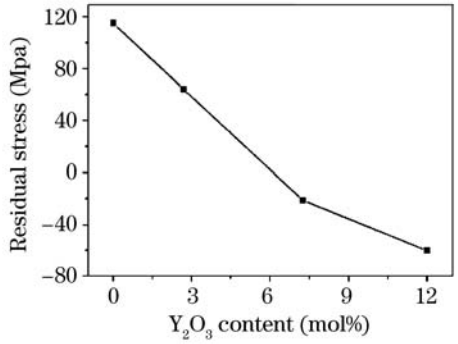

Fig. 3. Residual stress for different Y_2O_3 molar contents of YSZ thin films.

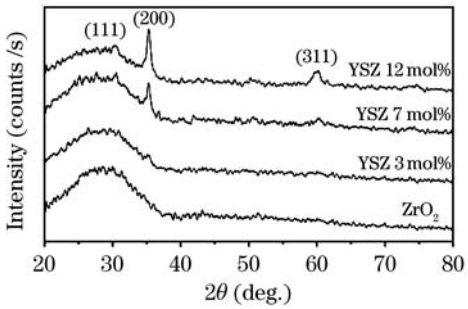

Fig. 4. XRD patterns of YSZ thin films with different Y_2O_3 contents.

compressive. Then the compressive stress increases to −60 MPa when the Y_2O_3 molar content increases further to 12 mol%.

XRD patterns of deposited samples for different Y_2O_3 dopant concentrations are shown in Fig. 4. When the dopant concentration is less than 3 mol%, no evident diffraction peak appears, indicating that the thin films are amorphous structures. When the dopant amount increases to 7 mol%, a diffraction peak appears at 35°, corresponding to the cubic crystal plane (200). Moreover, the diffraction peaks are weak and their intensities are low, which indicates that the thin films only crystallize partially and the main constituent of them is amorphous. When the Y_2O_3 molar content increases to 12 mol%, the YSZ thin film exhibits obvious crystallization. The peaks are approximately at 34.968°, 30.128°, and 59.848°, which are attributed to the diffraction of (200), (111), and (311) planes of cubic phase of ZrO_2, respectively.

The total residual stress σ in a thin film, which results from three major contributions, could be expressed as[14]

$$\sigma = \sigma_{th} + \sigma_i + \sigma_e, \tag{3}$$

where σ_{th}, σ_i, and σ_e are the thermal, intrinsic, and all extrinsic stresses, respectively. The intrinsic stress originates from various defects and the lattice mismatch between the film and substrate, and depends on the method of film preparation, deposition conditions, growth rate, nature of substrate, etc. The thermal stress is caused by the difference in thermal expansion coefficients between the films and the substrates and the temperature difference between the deposition temperature T_1 and

the ambient temperature T_0. It can be calculated by

$$\sigma_{\rm th} = \left(\frac{E_{\rm f}}{1-\nu_{\rm f}}\right)(a_{\rm f}-a_{\rm s})(T_1-T_0), \quad (4)$$

where $E_{\rm f}$ and $\nu_{\rm f}$ are Young's modulus and Poisson ratio of the film, $a_{\rm s}$ and $a_{\rm f}$ are the thermal expansion coefficients of the substrate and the film, respectively. In addition to the thermal stress and intrinsic stress, a third term named extrinsic stress may result from the absorption of water molecules in the pores and voids of the evaporated films during or at the end of the deposition steps. In this letter, it is noted that all samples are deposited at the same temperature, elastic constants of all samples are assumed to be the same, so the thermal stresses of all films are presumed to be the same. The thermal expansion coefficient of ZrO_2 thin films $a_{\rm f}$ (10.2×10^{-6} K^{-1}) is greater than that of the substrates $a_{\rm s}$ (7.1×10^{-6} K^{-1}), and the ambient temperature T_0 is lower than the deposition temperature T_1. The thermal stress obtained by Eq. (3) is tensile and the value is about 130 MPa. So the tensile residual stress in the pure ZrO_2 thin films can be explained as the contribution of thermal stress caused by the heating during deposition which comes from the energy transmission of the condensing particles and the radiation heat from evaporation source. As for other YSZ thin films with different Y_2O_3 molar contents, it seems that thermal stress is not the dominant factor on the residual stress, yet only a small fraction of the residual stress. The stress variation with the increase of Y_2O_3 molar content may be attributed to the difference of intrinsic stresses and extrinsic stresses. As shown in Fig. 3, it can be observed that the microstructure of YSZ thin films varies as the Y_2O_3 molar content increases, and the YSZ thin films transform from amorphous to high temperature phase with the increase of Y_2O_3 molar content. According to the model proposed by Klockholm, the stress generation is based on annealing and shrinkage of disordered material[15]. Therefore, when the structure of films becomes more ordered, the stress decreases and even varies from tensile to compressive state. On the other hand, considering that the dislocation caused by Y^{3+} in the crystallite is one of the formation factors of residual stress, the stress will vary with the increase of Y_2O_3content. In addition, the films deposited by electron beam-physical vapour deposition (EB-PVD) usually present columnar and porous structure. The voids between the columns adsorbing oxygen and water vapor from the atmosphere make the films show compression stress, this also benefits the tensile stress decrease.

In summary, the effects of Y_2O_3 dopant content on residual stress, structure, and optical properties of ZrO_2 thin films have been investigated. It is found that the residual stress in YSZ thin films varies from tensile to compressive and the value from 115 to −60 MPa. The addition of Y_2O_3 is beneficial to the crystallization of YSZ thin film and the microstructure transforms from amorphous to high temperature phase. The refractive index decreases with the increase of Y_2O_3 molar content. Additionally, the variations of residual stress and the shifts of refractive index can be attributed to the evolution of the film structure.

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