Surface & Coatings Technology 236 (2013) 405–409

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Novel fabrication of high-quality zirconia ceramic thin films by polyglycol-assisted spreading deposition

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ARTICLE INFO

Article history:
Received 28 June 2013
Accepted in revised form 14 October 2013
Available online 25 October 2013

Keywords:
Polymer precursor
Deposition
Zirconia
Thin film
Laminates

ABSTRACT

A polyglycol-assisted spreading deposition (PASD) method has been used to prepare the high-quality ZrO_2 thin film on single crystalline Si (111) substrate. The structure and composition of the films were studied by SEM, XRD and UV Raman techniques. Characterization results indicated that the ZrO_2 films were composed of nano-sized small particles and have a crack-free, dense and homogeneous microstructure. After a heat treatment of 10 min at 700–900 °C, the films showed a mixture of monoclinic and tetragonal ZrO_2 phases. And the grain sizes of monoclinic and tetragonal phases in the ZrO_2 films were 5–16 nm and 10–18 nm, respectively. In addition, the thin films of Y_2O_3-stabilized ZrO_2 (YSZ), $La_2Zr_2O_7$, and the multilayer thin films of $La_2Zr_2O_7$/YSZ were also fabricated by the PASD method.

1. Introduction

Zirconia (ZrO_2) ceramic thin film is used as a component in a wide variety of engineering applications such as catalysts [1], optical [2,3], solid-oxide fuel cell [4,5], thermal barrier coatings [6] and gas sensor [7]. In particular, ZrO_2 thin film is also an alternative gate dielectric in metal–oxide–semiconductor structure [8–11]. For all of these applications, the fabrication of high-quality ZrO_2 thin film has received steadily growing attentions. The techniques for the preparation of thin films include physical vapor deposition (PVD, e.g. thermal evaporation [12], pulsed laser deposition (PLD) [11,13] and sputtering [14]), chemical deposition (i.e. chemical vapor deposition (CVD) [6] and chemical solution deposition (CSD) [15,16]), polymer-assisted deposition (PAD) [17–19], and liquid phase deposition (LPD) [20–22].

Among these methods of growth ceramic thin films, the soft solution chemical approach (e.g. sol–gel method) is relatively simple, cost-effective, and is low in energy consumption since vacuum equipment is not required. Another advantage of this method is that the control of stoichiometry can be high [23]. In a typical sol–gel process, organic metal salt such as metal alkoxides is usually used as starting materials for preparing the precursor [19,24]. The precursor then undergoes a series of hydrolysis and condensation reactions to form a "sol" (colloidal suspension). Subsequently, the metal oxide thin film on substrate can be obtained from the spin-coating (or dipping) and thermal treatment processes [25,26]. The polymers such as citric acid [27], poly(vinyl alcohol, PVA) [28], poly(vinyl pyrrolidone, PVP) [26] and poly(ethylene glycol, PEG) [25,29,30] were frequently used in the precursor solution to form chelates between constituting cations in the polymer structure. For these polymers, the long chains of the PEG can play a bridging role and assist to form an M–O (M: metal) network in the precursor solution [25,30]. This ensures a homogeneous distribution of metal ions in the precursor solution, leading to the crack-free films.

However, the application of the sol–gel method for fabricating films on substrates with large-size or complex-shapes is limited, since a wafer spinning stage is involved in this process. As is well known, the ethanol has good wettability on the surface of various solids. If the hydrosolvent of the precursor solution for the sol–gel process is partially substituted by the ethanol, the surface tension of the precursor solution will be decreased, and this solution can spread out readily on the substrate. With the freely spreading out of the solution, the surface area increases. The ethanol volatilizes rapidly at room temperature, and leads the formation of a "gel" without spin.

In the present study, a PEG-assisted spreading deposition (PASD) method for preparing the high-quality ZrO_2 film from inorganic salt was established. The phase composition and microstructure of the ZrO_2 film were investigated. In addition, the abilities of achieving films with complex composition and structure are important to the utility of any film technique. Therefore, the thin films of 4 mol% Y_2O_3-stabilized ZrO_2 (4YSZ), 10 mol% Y_2O_3-stabilized ZrO_2 (10YSZ), $La_2Zr_2O_7$, and the thin film laminates of $La_2Zr_2O_7$/4YSZ were also fabricated by the PASD process.

2. Experimental

2.1. Preparation of thin films

For preparation of ZrO_2, 4YSZ, 10YSZ and $La_2Zr_2O_7$ thin films, 99.99% purity $Zr(NO_3)_4 \cdot 3H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ (Aladdin Chemistry Co. Ltd., Shanghai, China) were used as the starting materials

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http://dx.doi.org/10.1016/j.surfcoat.2013.10.025

and were dissolved in the deionized water. The total concentration of metal ions in the aqueous solution was 0.5 M. On the basis of the solution volume, 15 mg/mL PEG (molecular weight = 20,000) was added to aqueous solution. The solution was stirred with a magnetic stirrer to achieve complete dissolution.

The resulting solution (sol) was then mixed with absolute ethyl alcohol, the volume ratio between the sol and ethanol was 1:9. The final solution was dripped on a single crystal silica (111) wafer (RDS-80, RADOS Technology Oy, Turku, Finland; Φ = 100 mm) by using a pipettor (BIO-DL, Genex Beta, Torquay, UK; volume range: 10–100 μL). With the droplet spreading out, the ethanol volatilized quickly at room temperature. Subsequently, the Si wafer was pre-annealed at 550 °C for 5 min to achieve the decomposition of PEG, since the pyrolysis temperature of PEG is lower than 430 °C [25]. A schematic illustration of PASD process is shown in Fig. 1. The Si wafer used here was ultrasonically cleaned in dilute nitric acid and then thoroughly rinsed. The surface roughness of the Si wafer was determined by a surface roughness tester (Ra = 0.02 μm, NDT110, KaiDaKe instrument technology Co. LTD., Beijing, China).

Fig. 2 shows a plot of the film area as a function of the volume of ZrO_2 solution at room temperature, indicating that the area of film increases with increasing volume of the droplet. The data in Fig. 2 were obtained from the spreading process of ZrO_2 solution, each point was repeated for 10 times without pre-annealing, and the error bars represented the statistical errors. Fig. 2 showed that the films with areas in the range of 5 to 30 cm^2 could be prepared by modifying the volume of droplets. The amount of Zr deposited on the substrate for a single layer reached about 2.0×10^{-7} mol/cm^2. The thickness of single layer ZrO_2 film calculated from the molecular weight and the theoretical density was about 42 nm. For these results, the silicon wafers which have 3 cm × 3 cm of dimensions are used as the substrate for the film deposition in all the experiments described in this study. The films were coated for 10–20 layers from repeating the spreading and pre-anneal processes, and the films were then annealed 700–1000 °C for 10 min in air.

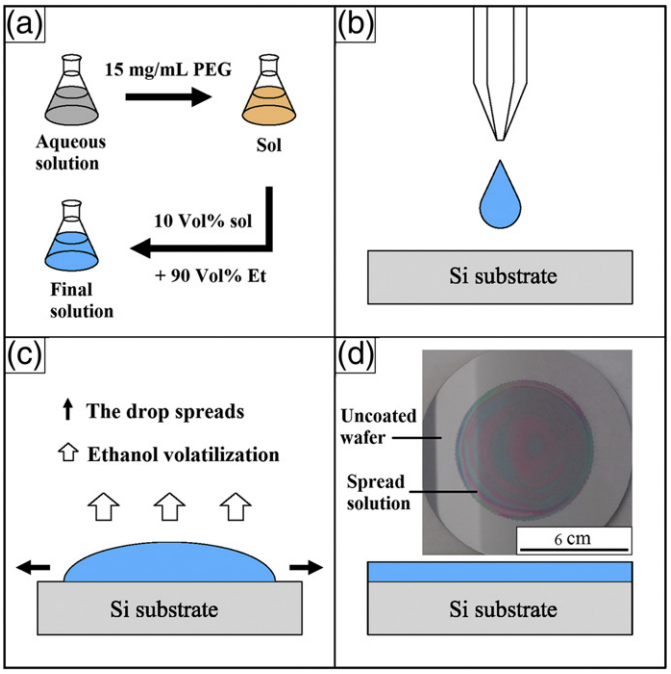

Fig. 1. A schematic illustration of PASD process: (A) the preparation of solution; (B) the drip addition of solution on Si substrate; (C) solution sprawling and ethanol volatilization; (D) a photograph of ZrO_2 film deposited for 1 layer without pre-annealing.

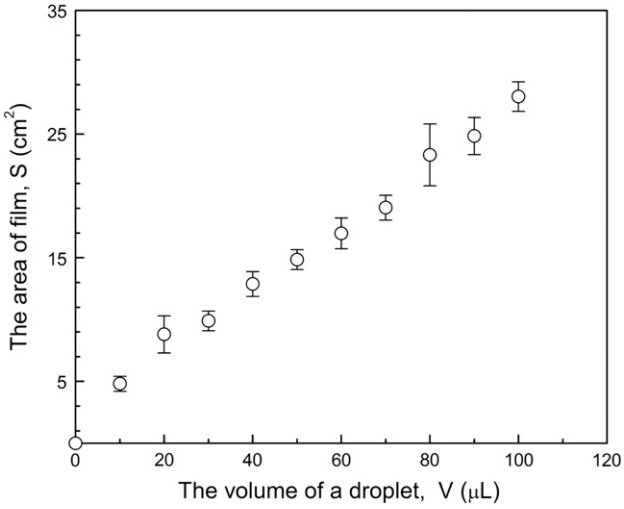

Fig. 2. The film area as a function of the volume of ZrO_2 solution at room temperature.

2.2. Characterization instruments

X-ray diffraction (XRD) analysis for the samples was carried out on an X'Pert PRO diffractometer (Cu Kα radiation, λ = 0.15406 nm; PANalytical, Almelo, Netherlands) equipped with thin film attachment. The grazing incident angle (α) of X-ray in the measurement for monolayer ZrO_2, 4YSZ, 10YSZ and $La_2Zr_2O_7$ films was 1.0°. And α = 0.5°, 0.8°, 1.0° and 1.2° for the $La_2Zr_2O_7$/4YSZ multilayer film were conducted to determine the structure of different depths of the film. Raman spectra were measured by an ultraviolet (UV) Raman spectrometer (Uv–Vis Raman System 1000, Renishaw plc, New Mills, UK), with a spectrum resolution of 1 cm^{-1}, and an excitation line of 325 nm. The surface and fractured cross-sectional morphologies of the films were observed using a field emission scanning electron microscopy (FE-SEM, Ultra 55, Carl Zeiss SMT Pte Ltd., Oberkochen, Germany) operated at 15 kV. The surface element distribution of the 4YSZ, 10YSZ and $La_2Zr_2O_7$ films was checked by an energy-dispersive spectrometer (EDS, Oxford IE450X-Max80) attached to the FE-SEM instrument.

3. Results and discussion

Fig. 3 shows the surface morphology of ZrO_2 films made from the sol modified with no-PEG and 15 mg/mL PEG, respectively. As shown in Fig. 3(a) and (b), after pre-annealing at 550 °C, the film prepared from no-PEG has a microstructure with a large volume of voids. In contrary, the film made from the PEG-modified sol showed a crack-free, dense and homogeneous microstructure. Fig. 3(c) and (d) shows the surface morphologies of ZrO_2 films (modified with 15 mg/mL PEG) after annealing at 800 °C and 900 °C for 10 min, respectively. The SEM images showed that the substrate was covered with small particles. The particle size of the films increased with increasing the annealing temperature. The SEM images also showed that the surfaces of the films were very smooth and free of cracks. The results indicated that the use of PEG could help in the improvement of the microstructure of thin films. As the gel was not formed in the film with no-PEG, the porous structure was caused by the decomposition of zirconium nitrate.

Fig. 4 is the fractured cross-sectional SEM images of ZrO_2 films on the single crystal Si substrate after annealing at 900 °C for 10 min in air. Fig. 4 revealed that the thicknesses of ZrO_2 thin films coated for 20 layers were about 723 nm. The thickness of single layer ZrO_2 thin film was in the range of 35–40 nm, in good agreement with the theoretical value (~40 nm) calculated from the data in Fig. 2. Fig. 4 also revealed that the film have a neat and dense cross-section.