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Effects of Thickness on the Electrical Conductivity of Sputtered YSZ Film with Nanocrystalline Columnar Microstructure

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Abstract: In order to investigate the effect of the thickness on the electrical conductivity of yttria-stabilized zirconia (YSZ) film, the nanocrystalline columnar-structured YSZ film with thickness of 0.67-2.52 μm was prepared by magnetron sputtering through controlling the deposition time. All the sputtered films with different thicknesses consist of the main phase of cubic YSZ as well as a small amount of monoclinic YSZ. The thicker films exhibit a typical columnar grain structure based on the fractured cross-sectional SEM observations. The average diameters of columnar grains increase from about 40 nm to 100 nm with the film thickness from 0.67 μm to 2.52 μm according to TEM analysis. The thinnest YSZ film with 0.67 μm thickness shows the highest apparent electrical conductivity in the four films in 400-800 ℃ due to the contribution from the highly conductive film/substrate interfacial region. On the other hand, the real electrical conductivities of YSZ films increase with film thickness from 0.67 μm to 2.52 μm after eliminating the contribution of the film/substrate interface. The increasing film thickness leads to the grain growth as well as the decrement in the volumetric fraction of the resistive columnar grain boundary and a consequent higher real electrical conductivity.

Key words: YSZ film; columnar microstructure; magnetron sputtering; interface effect; space charge effect

1 Introduction

Yttria stabilized zirconia (YSZ) has been widely applied as an excellent solid electrolyte in the fields of oxygen sensor and solid oxide fuel cell (SOFC) owing to its stable ionic conductivity in the reducing and oxidizing atmospheres[1]. However, the grain-boundary conductivity of polycrystalline YSZ is usually at least two orders of magnitude lower than that of the grain interior, resulting in the low total conductivity of polycrystalline YSZ[2,3]. As a result, the YSZ electrolyte is often prepared in the form of film or coating so as to reduce its resistance and ohmic polarization loss[4]. The physical vapor deposition (PVD), such as pulsed laser deposition, magnetron sputtering, electron beam evaporation, *etc*., is one of the most frequently-used processes for YSZ film preparation[5]. In the recent years, it has been the focus topic to explore the relationship between the microstructure and property of YSZ film prepared by PVD technique[6]. As an example, the effect of thickness on the electrical behavior of YSZ film has been widely discussed[7,8].

Although the theories of space charge effect and interfacial stress have been extensively employed to elucidate the electrical conduction behaviors of YSZ film, there is still much debate about the thickness effect on the electrical conductivity up to now[9-11]. For example, Kosacki I *et al* had prepared the highly textured YSZ film with thickness ranging from 15 nm to 2 μm. The in-plane conductivity measurement results demonstrated that the nanoscale effect with exceptionally high ionic conductivity only appeared in the film with thickness less than 60 nm. The increased conductivity was attributed to the significant contribution from the highly conductive film/substrate interface[12]. On the contrary, Guo X *et al* had deposited the polycrystalline YSZ film with thickness of 12-25 nm on (100) MgO substrate by pulsed laser deposition. The ionic conductivity of the nanostructured YSZ film was moderately decreased by about a factor of 4 compared with that of microcrystalline bulk ceramics, which was fully inter-

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preted based on the space charge effect theory[13].

In general, the variation in the electrical conductivity of YSZ film as a function of its thickness can be explained from the following two aspects. Firstly, the interfacial stress will change with the variation in film thickness, which exerts a great influence on the film/substrate interface and the electrical conductivity of YSZ films[14,15]. Jiang J *et al* had reported the evolutions of the conductivity with the YSZ film thickness and suggested that it was the tensile strain that contributed to the increased ionic conductivity of YSZ films[16]. Secondly, based on the space charge effect theory, the grain-boundary conductivity of polycrystalline YSZ is usually at least two orders of magnitude lower than that of the grain interior. So the increment in the volumetric fraction of the resistive grain boundary will lead to the decrement in the electrical conductivity of polycrystalline YSZ. As the grain sizes of YSZ films varied with their thicknesses, X. Guo insisted that the significantly high ionic conductivity could not be achieved in the nanostructured YSZ thin films[17].

In order to elucidate the relationship between the film thickness and electrical behavior systematically, the YSZ films with typical columnar microstructure and different thicknesses were prepared by radio frequency (RF) magnetron sputtering process in the present study. The relationship between the microstructure and the electrical conductivity of YSZ films was systematically explored.

2 Experimental

2.1 Film preparation

The YSZ films were prepared on the sapphire (0001) substrates by a RF magnetron sputtering equipment of JGP-450b made in China. A ceramic target with the chemical composition of $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ was sintered in air atmosphere at 1450 °C for 2 h using the powders with the same composition. The sputtering chamber was evacuated to a base pressure less than 10^{-5} Pa by a turbo molecular pump. The working pressure of argon gas was about 1.33 Pa during the sputtering course and the substrate temperature was maintained at 400 ℃ by a resistance heater. The film samples with different thicknesses were obtained through controlling the deposition time, *i e*, 30, 60, 120, and 240 min. Then the as-deposited films were annealed at 600 ℃ for 2 hours to relieve the interfacial stress between the films and substrates at a slow heating and cooling rate.

2.2 Microstructural characterization

The chemical and phase compositions of the sputtered films were analyzed by X-ray Fluorescence (XRF, Swiss ADVANTPXP-381) and X-ray diffraction (XRD, Bruker D8 ADVANCE) techniques, respectively. The XRD analysis was operated in the pattern of θ-2θ scan at 40 kV and 15 mA with Cu Kα radiation (1.54056 Å). The fractured cross-sectional morphologies of the films were observed using a JEOL Model JSM-840 scanning electron microscope. The grain sizes of YSZ films were analyzed by a Tecnai G2 F30 S-TWIN transmission electron microscopic (TEM) device and then calculated using the image analysis software of Image-Pro Plus.

2.3 Measurement of electrical conductivity

The AC impedance spectra of the YSZ films were collected with a SP-300 electrochemical workstation in the frequency range from 0.1 Hz to 2 MHz in the temperature range of 400-800 ℃ in dry air. The impedance data were fitted with a RC equivalent circuit model by Z-View software. At the same time, the DC conductivities were also measured by a Fluke multimeter in the same temperature range for comparison with the AC results. For the conductivity measurement, the etched hollow metal sheets with image reversal interdigital pattern and optimized geometry were employed to mask the film surface and then the gold electrodes with corresponding interdigital pattern were DC sputtered on top of the film utilizing a 99.99% pure gold target. The spacing between the interdigital electrodes was about 200 μm, at least two orders of magnitude larger than the film thickness, confirming that the measurement current could penetrate the entire film thickness and avoid the current constriction within several local grains. The silver wire was then connected to the gold electrode with the aid of a silver paste after sintering at 800 ℃.

3 Results and discussion

3.1 Microstructure of YSZ films

The XRD patterns of the four sputtered films with different deposition time are exhibited in Fig.1. All the films are composed of the main phase of the polycrystalline YSZ with cubic fluorite structure as well as a small amount of monoclinic YSZ phase. The broadening diffraction peaks appear in all the XRD patterns due to the fine grain microstructure of the YSZ films. The Scheller equation is not employed to estimate the grain sizes as the grains in the sputtered films are columnar, not equiaxial. So a further analysis on the fine grain structure of the four films has been conducted by the TEM observations. The preferred orientation growth characteristics vary with the deposition time or film thickness. For instance, the highly oriented growth of (111) plane appears in the thinner films deposited for 30, 60, and 90 min, while the thickest film sputtered for 120 min presents the oriented growth of (200) plane. In addition, the XRF analysis demonstrates that the chemical composition of the sputtered YSZ films is consistent with that of the corresponding ceramic target.

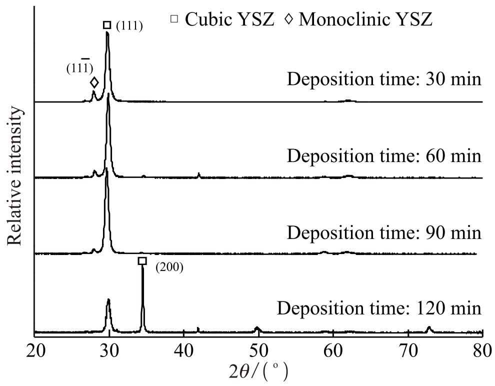


Fig.1 XRD patterns of the sputtered films with different deposition time

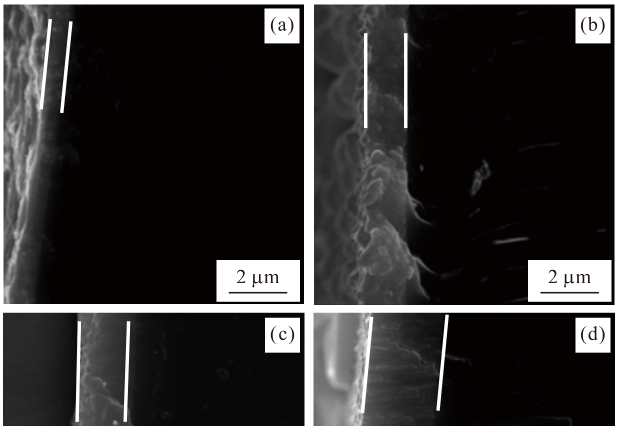


Fig.2 Cross-sectional SEM morphologies of the films with different thicknesses

The cross-sectional SEM morphologies of the sputtered films with different deposition time are shown in Fig.2. When the deposition time is set at 30, 60, 120, and 240 min, the corresponding thicknesses of YSZ films are 0.67, 1.47, 1.84, and 2.52 μm, respectively. All the films present a good adhesion to the substrates without any peeling. The thicker YSZ films, such as the 2.52 μm thick film, exhibit the typical columnar structure characteristic and the columnar grains are always aligned along the direction perpendicular to the substrate surface. The fine microstructure with the columnar grain characteristic for the 1.47 μm thick film was further characterized by TEM analysis as an example (Fig.3), in which the incident electrons were along the direction perpendicular to the cross section of the film. The average diameters of the columnar grains are about 55 nm for this YSZ film (Fig.3). It has been widely reported that the sputtered film evolves from an equiaxial grain structure to a columnar grain structure as its thickness increases from several nanometers to micrometers[18].

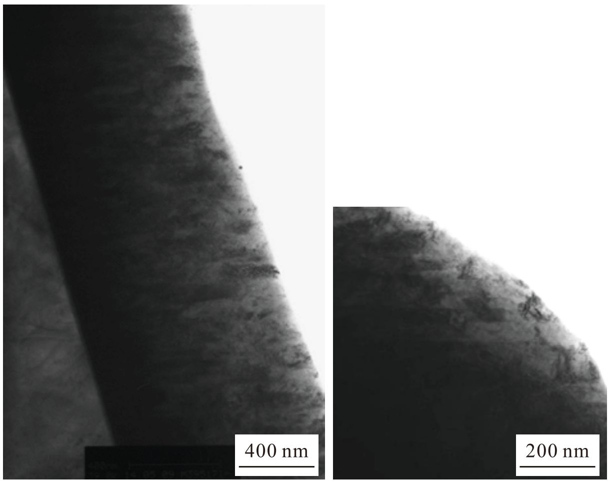
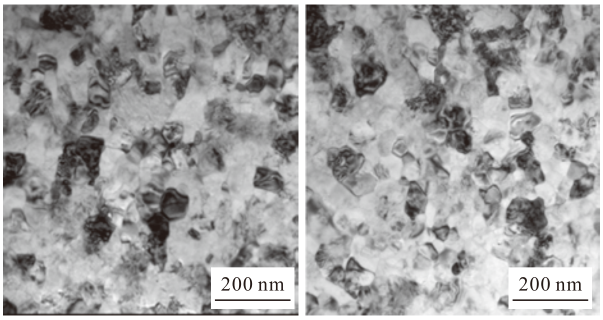
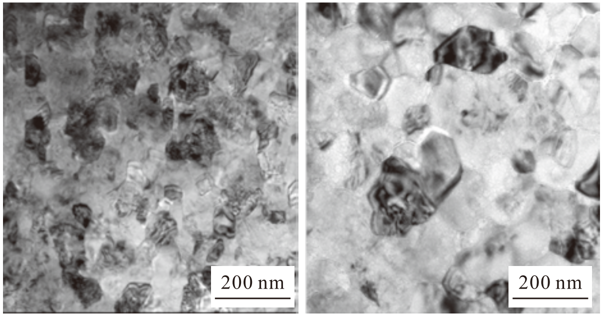


Fig.3 Cross-sectional TEM images of the 1.47 μm thick YSZ film



(a) Film with thickness of 0.67 μm (b) Film with thickness of 1.47 μm



(c) Film with thickness of 1.84 μm (d) Film with thickness of 2.52 μm

Fig.4 TEM observations on the grain sizes of different thick YSZ films

In order to elaborate the relationship between the film thickness and grain size, a TEM observation was conducted on the four sputtered films and the representative images of the films with thickness of 0.67, 1.47, 1.84, and 2.52 μm are shown in Fig.4 (a,b,c,d), respectively. In the TEM analysis, the incident electrons were projected along the direction perpendicular to the film surface, so the diameters, but not the heights, of columnar grains, were observed and then calculated using the software of Image-Pro Plus. According to Figs.4 (a,b,c,d), the average diameters of the columnar grains in the sputtered YSZ films with thickness of 0.67, 1.47, 1.84, and 2.52 μm are 40, 55, 80, and 100 nm, respectively. So, the diameters of columnar grains in the four sputtered films increase with increasing film thickness. According to the theory on the grain growth in the physically sputtered films, the columnar grains keep growing and their diameters increase correspondingly during the course of sputtering.

3.2 Electrical properties

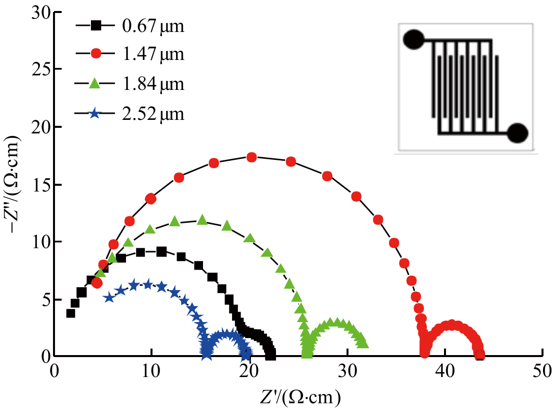


Fig.5 AC impedance spectra of different thick YSZ films at 400 ℃

The electrical conductivities of YSZ films with different thicknesses were measured by AC impedance and DC technique at 400-800 ℃. Fig.5 shows the typical AC impedance spectra of YSZ films at 400 ℃ as an example. There are two arcs in Fig.5. The left high frequency arc with a very low capacitance (C_g) is attributed to the grain impedance of the YSZ film, while the right low frequency one originates from that of the grain boundary with a relatively higher capacitance (C_{bg})[19]. As the measurement temperature rises beyond 600 ℃, the grain and grain-boundary impedances of YSZ film can not be distinguished due to the variations in C_g and C_{bg} with temperature as well as the presence of the stray capacity from the sapphire substrate, which is several orders of magnitude higher than C_g and C_{bg} of YSZ film[20]. So only the total conductivities are obtained by the AC impedance technique when the measurement temperature is higher than 600 ℃. Furthermore, the total conductivities measured by DC and AC techniques are compared with each other, and both of them demonstrate a good consistency.

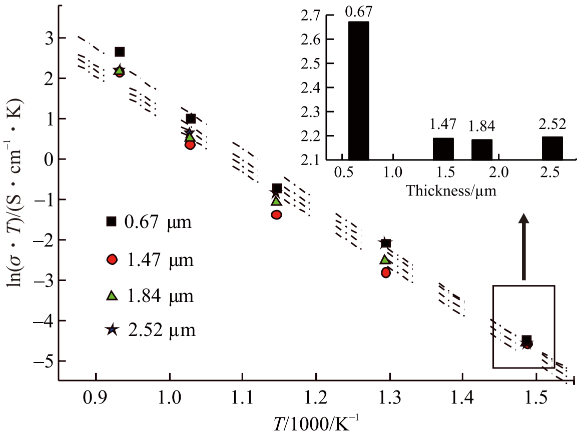


Fig.6 Arrhenius plots of the total apparent electrical conductivities of YSZ films with different thicknesses

Then the apparent total electrical conductivities of YSZ films with different thicknesses are exhibited in the typical form of Arrhenius plots in Fig.6. The 1.47, 1.84, and 2.52 μm thick films present similar electrical conductivities at 400-800 ℃, which are significantly lower than those of the 0.67 μm thick film in the whole measurement range. It has been reported by many studies that the apparent conduction behaviors of YSZ film are always controlled by both the YSZ film itself and the film/substrate interface region. For example, Igor Kosacki *et al* had prepared the YSZ films with thickness below 60 nm on MgO substrates and an in-plane conductivity enhancement had been observed for the films, which was attributed to the transition from lattice to interface controlled diffusivity[21]. In general, it had been deduced by Kosacki that the thickness of the interface region was about 1.6 nm and its electrical conductivity was 3-4 orders of magnitude higher than that of the lattice of YSZ film[22]. Obviously, the volumetric ratios of interface region to film are always decreasing with increment in film thickness and the contribution from the YSZ/substrate interface region is weakened with increasing film thickness correspondingly. So the thinnest film with thickness of 0.67 μm shows the highest apparent conductivities compared with the other three thicker samples.

Based on the analysis above, the measurement results of the apparent electrical conductivities of YSZ films are decisively affected by the film/substrate interfacial behaviors. However, the apparent electrical conductivity does not represent the real ionic conduction characteristics of the YSZ films themselves, but a mixed conduction behaviors of both the films and interfacial regions. In order to elucidate the effects of thicknesses and grain sizes on the electrical conductivities of YSZ films clearly and accurately, it is necessary and beneficial to eliminate the contribution from the film/substrate interface region and obtain the real electrical conductivities of YSZ film itself.

According to the mixture rule of two resistors in an ideal parallel connection, the apparent conductivity can be represented by[23]:

$$\sigma_{\rm a}=\sigma_{\rm f}(1-f_{\rm i})+\sigma_{\rm i}f_{\rm i} \qquad (1)$$

where, $\sigma_{\rm a}$ is the apparent conductivity, $\sigma_{\rm f}$ is the film conductivity, $\sigma_{\rm i}$ is the interfacial conductivity, and f_i is the volumetric ratio of interfacial region to the whole film. As mentioned above, the thickness of the interface region is about 1.6 nm and its electrical conductivity is 3-4 orders of magnitude higher than that of the film. Then using the equation (1), the real conductivities ($\sigma_{\rm f}$) of YSZ films with different thicknesses are obtained and exhibited in Fig.7 in the typical form of Arrhenius plots. It is obvious that the real electrical conductivities of YSZ films tend to increase with the increment in film thickness after the interfacial effects are eliminated.

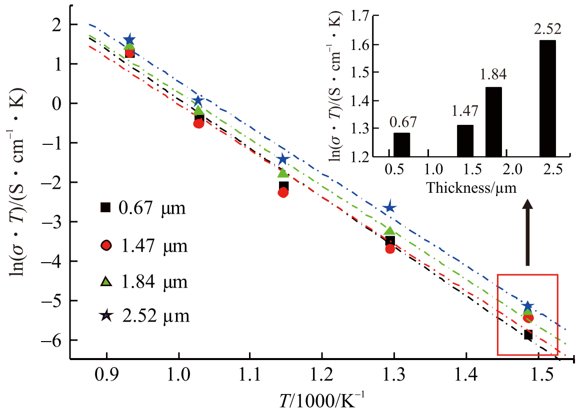


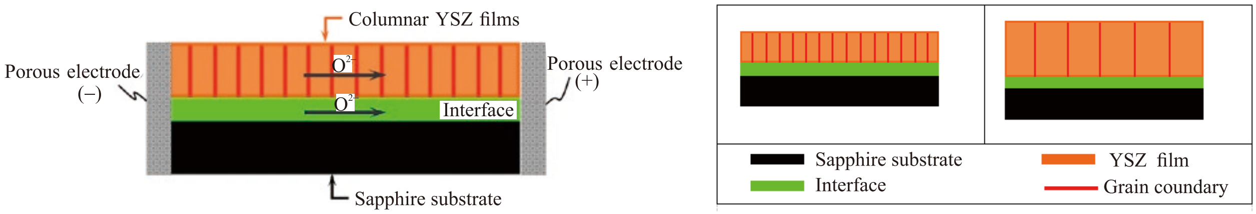
Fig.7 Arrhenius plots of the total real electrical conductivities of YSZ films with different thicknesses

Based on the space charge effect theory, the grain-boundary region of polycrystalline YSZ ceramic consists of a grain-boundary core and two adjacent space-charge layers. The grain-boundary core of YSZ is positively charged probably due to the oxygen deficiency or the oxygen vacancy enrichment there. So the oxygen vacancies are depleted in the space-charge layers and the grain-boundary regions are blocking the oxygen-ion conduction, leading to a low conductivity of the grain boundary region. In the present study, the grain sizes of YSZ films increase with the increment in film thicknesses, just as shown in Fig.4. Correspondingly, the volumetric ratios of the resistive grain boundary will decrease with the increment in film thicknesses, leading to the increment in the electrical conductivities of the films. So the real conductivities of YSZ films increase with the increment in film thickness, opposite to the trend of the apparent conductivity. As described above, the effects of thickness on the grain size and electrical conductivity of the sputtered films have been illustrated in Fig.8.

In 2011 X. Guo reviewed the possibility about achieving the significantly higher ionic conductivity in nanostructured zirconia-based ceramics or thin films. According to the literature, the decreased ionic conductivity is mostly observed in nanostructured ZrO_2 ceramics compared with the mirometer-sized ceramics[24]. Some occasional enhanced conductivity in the nanostructured thin films can also be attributed to the film/substrate interfacial contributions due to the lattice mismatch or space charge effects[25].

4 Conclusions

The nanocrystalline columnar-structured YSZ films with 0.67-2.52 μm thickness were prepared by RF magnetron sputtering. The sputtered films mainly consist of cubic YSZ and a small amount of monoclinic YSZ. The average diameters of the columnar grains increase from about 40 nm to 100 nm with increasing film thickness from 0.67 μm to 2.52 μm. The thinnest YSZ film, *i e*, the 0.67 μm-thick film, exhibits the highest apparent electrical conductivity at 400-800 ℃ compared with the other three thicker ones, which is



(a) Schematic of electrical conductivity measurement

(b) The grain growth with film thickness

Fig.8 The effects of thickness on the grain size and electrical conductivity of the sputted films attributed to the contribution from the high conductive film/substrate interface. After eliminating the effects of the film/substrate interface, the real conductivity increases with the increment in film thickness, and the volumetric fractions of the resistive grain boundary region decrease with increasing film thickness and grain growth.

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