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Effects of substrate temperatures on the crystallizations and microstructures of electron beam evaporation YSZ thin films

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ABSTRACT

Yttria-stabilized zirconia (YSZ) thin films were grown on Si(1 0 0) substrate using electron beam (E-beam) evaporation by changing the substrate temperature from room temperature (RT) to 250 °C. Effects of different substrate temperatures on the crystalline structure, the lattice constant, the grain growth, and the strain of YSZ thin films and the thickness of interfacial SiO_x layer between Si wafer and YSZ thin films were developed. Even depositing at room temperature, X-ray diffraction (XRD) analyses showed that the reflection peaks of (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes were formed. The relative reflection intensities of (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes were changed as the different substrate temperatures were used. The strains of YSZ thin films increased with increasing substrate temperature and reached a minimum value at 200 °C. The amorphous interlayer formed between Si wafer and YSZ thin films and the images of lattice mismatch were also analyzed by using high resolution transmission electron microscopy (HRTEM).

1. Introduction

Solid oxide fuel cell (SOFC) was a friendly low pollution energy conversion device that could convert the energy of a chemical reaction directly into electrical energy [1]. Yttria-stabilized zirconia, YSZ, had widely been used as an electrolyte in SOFC stack [2–4]. Except the single-layer YSZ thin film, many YSZ-based multi-layer thin films were also developed for the different applications of SOFC devices, for example, Ni-$Sm_{0.2}Ce_{0.8}O_{1.9}$ anode-supported YSZ electrolyte films [5], double layer thermal barrier coating $La_2Zr_2O_7$–YSZ thin films [6], $Ni_{1-x}Fe_xO$–YSZ thin films for intermediate temperature anode [7], and $La_{0.7}Ca_{0.3}CrO_{3-\delta}$–YSZ for the simple SOFCs [1]. Except the Y_2O_3 was used to stabilize the zirconia (ZrO_2) [8,9], other oxides were also added into YSZ to develop their properties, for example, La_2O_3 in YSZ [10] and Sm-doped CeO_2 in NiO/YSZ anode [11]. At the same time, YSZ thin films prepared onto Si substrate had many potential applications, such as buffer layer for epitaxial growth of oxide electrode [12], superconductors [13], and capacitors [14]. To integrate those oxide hetero-structures on Si was very important since current semiconductor and integrated device technologies heavily relied on the depositing technologies of thin films. For that, many different thin film processing techniques were developed to prepare single-layer YSZ thin film or multi-layer YSZ-based thin films, such as ion-beam sputtering, RF sputtering, electrophoretic deposition, electrostatic spray deposition, pulsed laser deposition, and metal organic chemical vapor deposition. Significantly, electron beam (E-beam) evaporation [15,16] offered two major advantages for the thin film deposition. First, a high density power was used as the power source and an easy thickness control was achieved on the depositing rates. And second, the surface area of deposited thin films showed a high temperature, hence, the deposited thin films would crystallize as the substrate was not heated.

E-beam evaporation represented a realizable fabrication technique in that it was based on a molecular deposition of components, thus leading to continuous thin film orientation. Moreover, metallurgical reactions between substrate and source materials leading to thin film contamination were therefore minimized. The orientation of YSZ thin films strongly depended on the depositing parameters and nucleation-heated methods during the depositing processes [17–19] and, further, influenced their applications. In this study, we would use the E-beam evaporation to deposit YSZ thin films on Si(1 0 0) and investigate the effects of substrate temperature on the characteristics of YSZ thin films. For E-beam evaporation, the effects of Y_2O_3 content on the grown and structural characteristics of YSZ thin films prepared at 200 °C had been reported by Wu et al. [15] and Hartmanova et al. [16]. However, they did not study the effects of substrate temperatures on the growth

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characteristics in detail. Suh et al. [20] indicated the substrate temperatures had large influences on the crystalline orientations of deposited thin films and the formations of interfacial layers. We had found that even the substrate was unheated, the orientation peaks of YSZ thin films were formed. We would show that the substrate temperature played an important role in nucleation and relatively crystalline intensities of orientations in YSZ thin films. We would also show that the substrate temperature had large influences on the lattice constants and strains of YSZ thin films. High resolution transmission electron microscopy (HRTEM) was used to analyze the lattice defects and the variations of interfacial layers. We could use the analyzed data to demonstrate the phenomena for the variations of crystallization of YSZ thin films and to find the thickness of interfacial layer between the YSZ thin films and Si(1 0 0) substrate.

2. Experimental procedures

YSZ polycrystal, zirconia with 8 mol% Y_2O_3, with purity higher than 99.9% was synthesized from a powder supplied by Tosoh Co. Ltd., Tokyo, Japan. In order to obtain the disks used as the source material for E-beam evaporation, the powder was pressed and sintered at 1400 °C for 4 h. The Si(1 0 0) substrate was cleaned in isopropyl alcohol (EPA) and deionized water and dried by nitrogen gas. A vacuum system with 5×10^{-6} Torr was used as base pressure and for deposition, oxygen was introduced into the chamber to adjust the working pressure of 1×10^{-5} Torr. During the depositing process, substrate was hold with a working distance of 20 cm and heated by irradiation at 100 °C, 150 °C, 200 °C, and 250 °C, respectively. The deposition rate of YSZ thin films was controlled by the power of E-beam and monitored by a thickness control system (CRTM-6000, ULVAC, Japan). The crystalline structure of YSZ thin films was identified by XRD with Cu Kα. The thickness and surface observation of YSZ thin films were characterized by field emission scanning electron microscopy (FESEM) and the micro structural analyses were done using HRTEM.

3. Results and discussion

The thicknesses of YSZ thin films deposited under different substrate temperatures are observed from the cross-section images of FESEM and the results are shown in Fig. 1, the thicknesses for all samples are about 500 nm. As the cross micrographs shown in Fig. 1 are compared, there are different results as the substrate temperature is changed. As the substrate temperature increases from RT to 200 °C, the YSZ thin films grow like a bar or a disk along the up direction. But depositing at 250 °C, the bar- or disk-shaped growths are transformed into the handstand-triangle disk. Fig. 1 also shows that the interfacial layers (the SiO_x layer shown in Fig. 5) between YSZ thin films and Si substrate become un-apparently as the substrate temperature increases. Those results suggest that the YSZ thin films have differently crystalline orientation and leading to different texture coefficients, that will be shown in Figs. 2 and 3. Also, the substrate temperature has large influences on the characteristics of epitaxial growth YSZ thin films and the interfacial layer.

The XRD patterns of YSZ thin films on Si(1 0 0) substrate deposited under different substrate temperatures are shown in Fig. 2. The reflection peaks of (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes are found in all YSZ thin films and the crystalline YSZ fluorite structure is obtained, even without external heating is used. In general, the mobile energy of YSZ thin films is highly dependent on the depositing parameters. For that, the orientation of YSZ thin films also strongly depends on the substrate condition used during the depositing processes, especially on the substrate temperature. Because lower substrate temperature means lower mobile energy supplied for absorbed species and amorphous thin films are obtained [21]. However, the crystalline YSZ thin films are obtained and the reflection intensity of (2 2 0) plane obviously increases with increasing substrate temperature. In case of YSZ thin films, the (1 1 1) plane has the lowest surface energy. Thus, preferential (1 1 1) out-of-plane orientation is developed under the substrate temperature of 250 °C and the YSZ thin film has the different grain growth shape or direction, as the cross morphologies shown in Fig. 1.

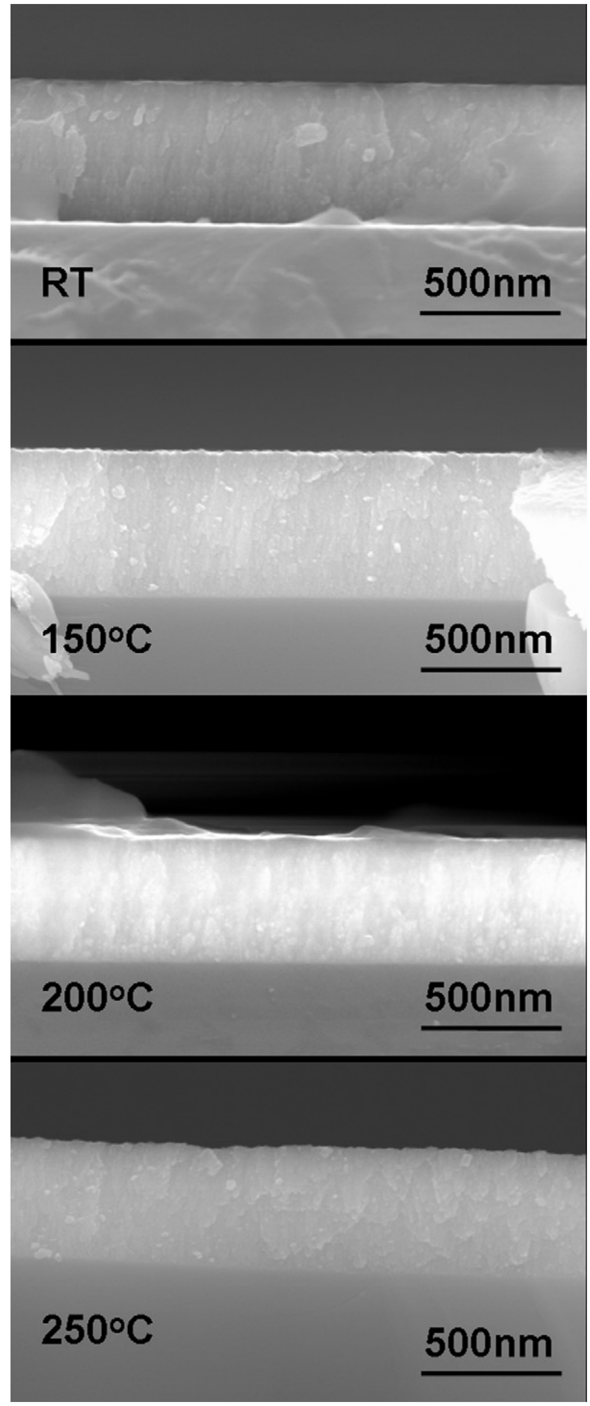

Fig. 1. Cross-section images of YSZ thin films deposited under different substrate temperatures.

In Fig. 2, the reflection intensity of (2 0 0) plane reveals a maximum value at 200 °C. Crystallographic texture of YSZ thin films is referred and texture coefficient (TC) is used to describe the textures of thin films with Eq. (1) [22]:

$$TC_{h\,kl} = \frac{I_{hkl}/I^o_{hkl}}{1/n \sum I_{hkl}/I^o_{hkl}} \quad (1)$$

where I_{hkl} is reflection intensity of (hkl), I^o_{hkl} is standard reflection intensity of (hkl) reported in JCPDs card (No. 82-1246), n is number of reflection peaks. The TC values of various reflections of YSZ thin films shown in Fig. 3 indicate that the (2 0 0) plane pos-