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Short communication

Effects of the oxygen pressure on the crystalline orientation and strains of YSZ thin films prepared by E-beam PVD

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Abstract

Yttria−stabilized zirconia, YSZ, thin films were prepared by E-beam physical vapor deposition (PVD) at 200 °C under oxygen pressure of 1×10^{-3}∼1×10^{-5} Torr. Observations by Field Emission Scanning Electron Microscope (FESEM) proved that different oxygen pressures influenced the thickness of interfacial SiO_x layer formed between the YSZ thin films and Si(100)-substrate. X-ray diffraction (XRD) patterns were used to determine the crystalline structure and calculate the surface grain size of deposited YSZ thin films. XRD patterns also showed that the peaks corresponding to planes (111), (200), (220), and (311) were found and the YSZ thin films revealed the fluorite structure. At lower oxygen pressure (1×10^{-5}∼1×10^{-4} Torr) YSZ thin films revealed the (111) preferred orientation and at higher oxygen pressure (5×10^{-4}∼1×10^{-3} Torr) YSZ thin films revealed the (200) preferred orientation. The effects of oxygen pressure on the lattice constants and the internal strains of YSZ thin films were also investigated.

Keywords: A. Films; B. Interfaces; Yttria-stabilized zirconia

1. Introduction

Yttria−stabilized zirconia (YSZ) thin films wildly used as an electrolyte in solid oxide fuel cell stack for power generation application. At the same time, the YSZ thin films prepared onto Si substrate have many potential applications, such as buffer layer for epitaxial growth of oxide electrodes [1], superconductors [2], and capacitors [3], etc. It is of interest to integrate those oxide hetero-structures on Si substrate since current semiconductor and integrated device technologies heavily rely on Si process technology. YSZ thin films can be prepared by a variety of processing techniques, such as, E-beam or pulsed laser evaporation and vapor deposition (PVD), RF sputtering, electrophoretic deposition, and metal organic chemical vapor deposition. Significantly, E-beam PVD offers two major advantages: (1) a high power density and hence a wide range of control over evaporation rates and (2) the source material for evaporation being contained in a water-cooled crucible and its surface area showing a high temperature [4,5]. Metallurgical reactions between substrate and deposited materials leading to film contamination are therefore minimized. Moreover, E-beam PVD represents an available fabrication technique in that it is based on a molecular deposition of components, thus leading to continuous film formation.

The growth orientations of the YSZ thin films strongly depend on the condition used during the nucleation step, namely deposition parameters and the characteristics of used substrates [6,7]. Park et al. [8] reported YSZ deposited on various Ni substrates to result in thin films with either peaks corresponding to planes (111) and (002) or mostly plane (111). Wu et al. [4] pointed out the maximum diffraction peak to be in the crystal plane (200) for YSZ thin film with 7 mol% Y_2O_3 deposited at 350 °C. Hata et al. [9] prepared YSZ thin films on Si(100), Si(110), and Si(111) substrates by RF sputtering and concluded that YSZ orientation was properly controlled by substrate surface in the cases of Si(100) and Si(111). For E-beam evaporation, the effect of Y content on the growth characteristics and structural characteristics of YSZ prepared at 200 °C have been reported by Wu et al. [5] and Hartmanova

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et al. [10]. Mahieu et al. deposited the YSZ thin films at the oxygen pressure of 1×10^{-3} Torr, the oriented crystallization of plane (111) was improved [11]. However, they did not discuss the effects of oxygen pressure on the oxidation of Si(100) substrate and then the effects on the oriented crystallization. In this study, the effects of oxygen pressure on structure and morphology of YSZ thin films are investigated. We will show that the oxygen pressure has large influences on the thickness of SiO_x layer on the surface of Si-substrate and then also on the oriented crystallization of YSZ thin films.

2. Experimental details

YSZ polycrystals (8% mol Y_2O_3, purity higher than 99.9%) were synthesized from a powder supplied by Tosoh Co. Ltd., Tokyo, Japan. In order to be used in the E-beam evaporation process, the YSZ power was pressed into disks and sintered at 1400 °C for 4 h. The silicon(100) substrate was cleaned in isopropyl alcohol (EPA) and deionized water and dried by nitrogen gas. Acid-etching process on native Si wafer prior to deposition was conducted to remove the residual SiO_2 from its surface. A vacuum system with a base pressure of 5×10^{-6} Torr was used as base pressure, then oxygen was introduced into the chamber to adjust the working pressure. Substrates were fastened in a curved holder with a working distance of 20 cm and heated by irradiation to 200 °C. In order to find the influences of oxygen pressures on the crystallizations of deposited YSZ thin films, the working pressure was changed from 1×10^{-5} to 1×10^{-3} Torr (detected by ion gauge). The deposition rates of YSZ thin films were controlled by an E-beam power (ULVAC, type EGK-3 M) and monitored by a thickness control system (CRTM-6000, ULVAC, Japan). The thickness and surface observation of YSZ thin films were characterized by Field Emission Scanning Electron Microscope (FESEM). The crystalline structures of YSZ thin films were identified by X-ray diffraction (XRD) patterns with Cu Kα1. The micro structural analyses were done using High Resolution Transmission Electron Microscopy (HRTEM).

3. Results and discussion

The cross section images of YSZ thin films deposited under different oxygen pressure are observed by FESEM and shown in Fig. 1, the thickness for all samples is about 500 nm. As the oxygen pressure increases from 1×10^{-5} to 1×10^{-3} Torr, the cross topographies are changed from the handstand-triangle disk (Fig. 1(a)) to disk-shaped growth (Fig. 1(b) and Fig. 1(c)). The results in Fig. 1 also show that the thickness of interfacial SiO_x layer between YSZ thin films and Si substrate increases with increasing oxygen pressure. As the oxygen pressure increases from 1×10^{-5} to 1×10^{-3} Torr (Fig. 2), the YSZ thin films also reveal different surface morphologies. At lower working pressure of 1×10^{-5} Torr (Fig. 2(a)), the larger particles are observed and the particles agglomerate together. As the working pressure increases from 1×10^{-5} to 1×10^{-3} (Figs. 2(a), 2(b), and 2(c)), the particle size decreases. These results suggest that the YSZ thin films have different crystalline orientations that will lead to different texture coefficients, as shown in Fig. 4.

The XRD patterns of YSZ thin films prepared at various oxygen pressures are shown in Fig. 3. The existences of diffraction peaks of planes (111), (200), (220), and (311) demonstrate that YSZ thin films are the fluorite structure and oxygen pressure plays an important role in nucleation of YSZ thin films on Si(100) substrate. The peak of plane (200) is the preferred orientation at lower pressure of $1 \times 10^{-5} \sim 1 \times 10^{-4}$ Torr, while and peak of (111) plane is preferred orientation at higher pressure of $5 \times 10^{-4} \sim 1 \times 10^{-3}$ Torr. The diffraction intensity of plane (111) obviously decreases with increasing oxygen pressures, while the inverse tendency is found for that of plane (200). Crystallographic textures of YSZ thin films referred to the texture coefficients (TC) of YSZ thin films can be calculated by using Eq. (1) [12]:

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

Where I_{hkl} is the reflection intensity of (hkl), I^o_{hkl} is the standard reflection intensity of (hkl) reported in JCPDs card, and n is the number of reflection peaks.

Fig. 4 indicates that the plane (200) possesses the highest TC value at the oxygen pressure of $5 \times 10^{-4} \sim 1 \times 10^{-3}$ Torr. Hata et al. showed a lattice model to demonstrate that the peak of plane (200) was the preferred orientation on Si(100) substrate and the peak of plane (311) had the lowest TC value [9]. The results developed by Wu et al. [4] and Hata et al. [9] agree with our results as the oxygen pressure is equal to and higher than 1×10^{-4} Torr. The TC value of plane (200) decreases and that of plane (111) increases as the oxygen pressure is higher than 1×10^{-4} Torr. Because the thickness of SiO_2 layer increases

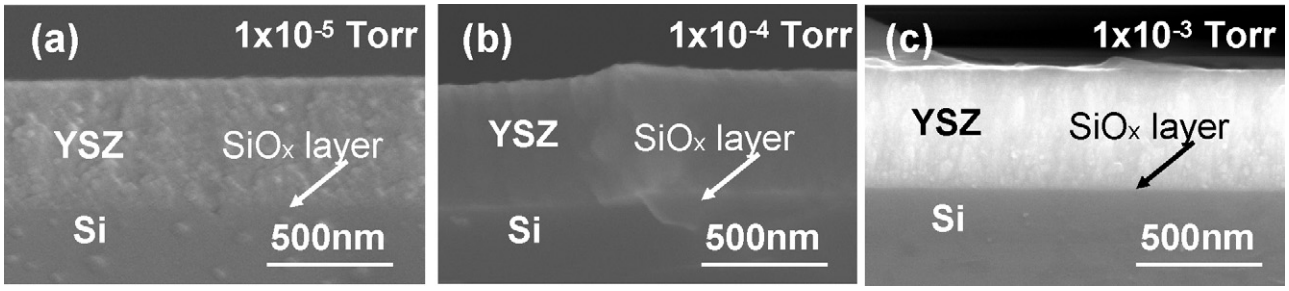

Fig. 1. Cross section images of YSZ thin films prepared at different oxygen pressures (SEM).

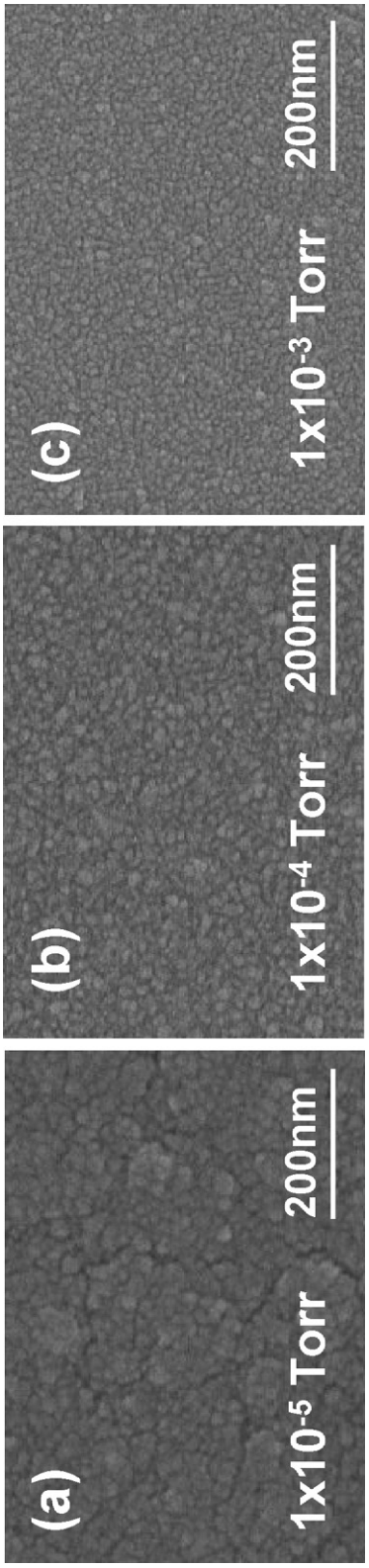

Fig. 2. Micrographs of YSZ thin films prepared at different oxygen pressures.

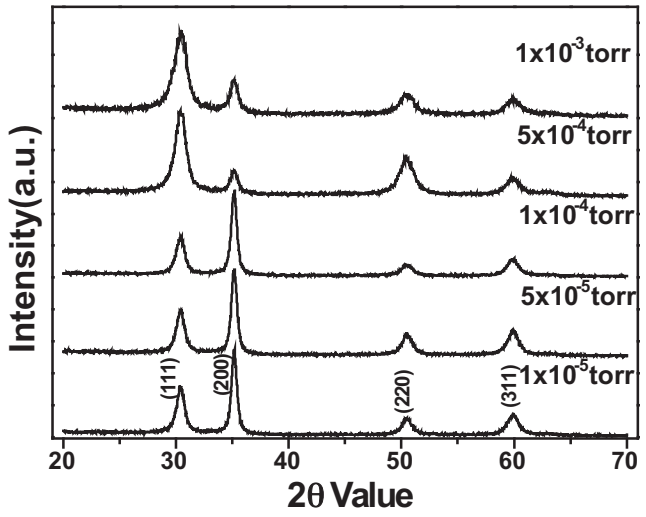

Fig. 3. XRD patterns of YSZ thin films deposited at different oxygen pressures.

with increasing oxygen pressures, the YSZ thin films cannot grow directly on Si(100) substrate.

Chow and Wang [13] reported that no interfacial layer was found in YSZ thin films prepared by PLD under 3.75×10^{-6} Torr. The phenomena are that Zr ions absorb oxygen ions from SiO_x layer on the surface of Si wafer, reducing SiO_2 to SiO. SiO decomposition is expected as lower oxygen partial pressure is used, as a result, the thickness of SiO_x layer is reduced. From the observation by HRTEM (not shown here), the thickness of SiO_x layer has become thicker as higher oxygen pressure is used. The increase in the thickness of interfacial SiO_x layer is related to the increase of the oxygen absorbing efficiency of Zr ions. The SiO_x layer is thinner as lower oxygen pressure is used, for that the YSZ thin films can epitax according the orientation of Si(100) wafer and the (200) orientation has the higher TC value. When the oxygen pressure increases, YSZ thin films will crystallize in according to the lowest surface energy of plane (111) and the crystalline intensities of other planes will decrease. When the oxygen

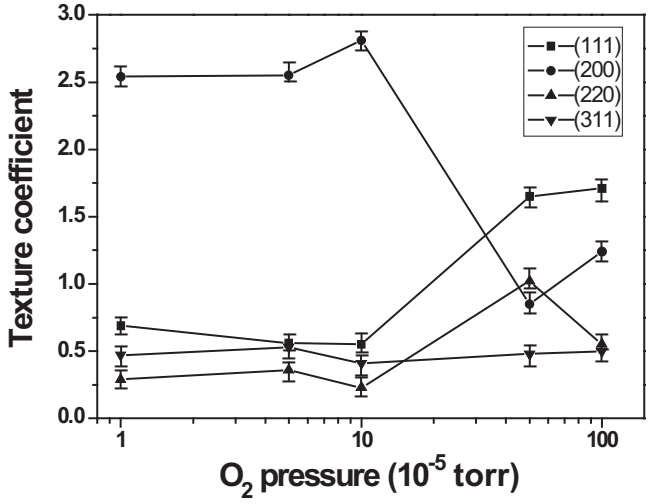

Fig. 4. Dependence of TC values of YSZ reflections deposited at different oxygen pressures.

pressure is 1×10^{-3} Torr, the plane (111) has the largest oriented crystallization and TC value [11].

The relationships between lattice strain (η) and full width at half maximum value (FWHM, β) can be expressed as Eq. 4 [14]:

$$\beta\cos\theta/\lambda = 2\eta\sin\theta/\lambda + 1/d \quad (2)$$

Where θ is a Bragg's angle, λ is the wavelength of X-ray, and d is the crystallite size. The 2η and $1/d$ could be separately obtained by calculating the slope and intercept of profile of $\sin\theta/\lambda$ versus $\beta\cos\theta/\lambda$. The strain reveals a minimum value at 1×10^{-5} Torr and then increases as the depositing pressure is increased to 5×10^{-5} Torr. The Nelson–Riley function can be utilized to determine the lattice constants because of the minimizing effect of stress [15]:

$$\Delta d/d = K(\cos^2\theta/\sin\theta + \cos^2\theta/\theta) \quad (3)$$

Where d is plane space, Δd is the difference of plane space, K is constant, and θ is diffraction angle. In this method, the following equation is used to obtain the lattice constants:

$$a = a_0 + a_0 K'(\cos^2\theta/\sin\theta) \quad (4)$$

Fig. 5 shows the dependences of grain size on oxygen pressure illustrated from Eq. 2. The grain size decreases with increasing oxygen pressure and reaches the minimum at $5\text{x}10^{-5}$ Torr. However, the phenomena for the decrease of grain size are believed to be caused by the change of mainly crystalline orientation, as shown Figs. 3 and 4. As Fig. 6 shows, the lattice constant calculated from the XRD patterns (a) and the real lattice constant (a_0) are 0.51538–0.51567 nm and 0.5130–0.51503 nm, respectively. Fig. 6 also shows that the larger difference between a and a_o has led to larger strain. The variations and differences in the a and a_o values are caused by the differently oriented crystallizations and strains. Fig. 6 also shows the dependence of strain on depositing pressure illustrated from Eq. (4). As expectation, the crystallization

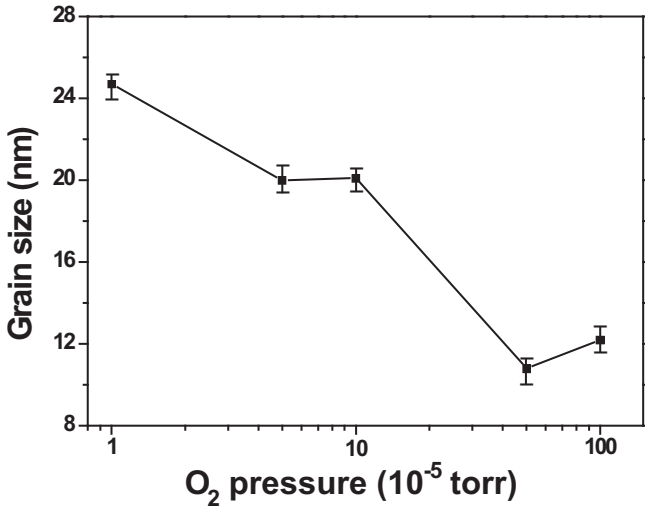

Fig. 5. Grain sizes of YSZ thin films deposited at different oxygen pressures.

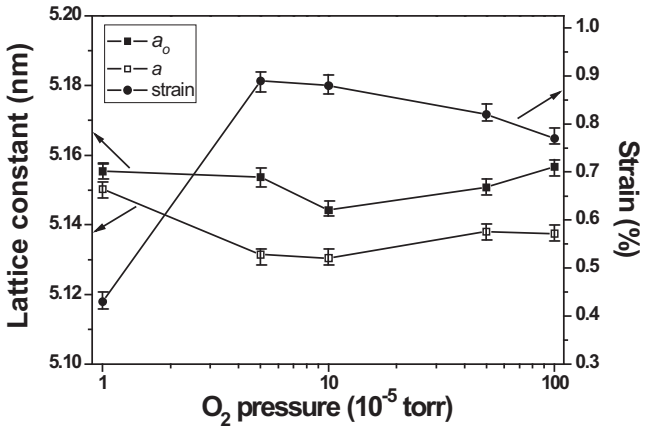

Fig. 6. Lattice constants and film strains of YSZ thin films deposited at different oxygen pressures.

has smaller strain value as the difference between a_o and a (so called "lattice distortion") is smaller.

The HRTEM images are taken from the [111] direction axis, as Fig. 7 shows, the lattice clearly appears cubic and continuant. The maximum lattice deviations for 1×10^{-3} Torr-deposited

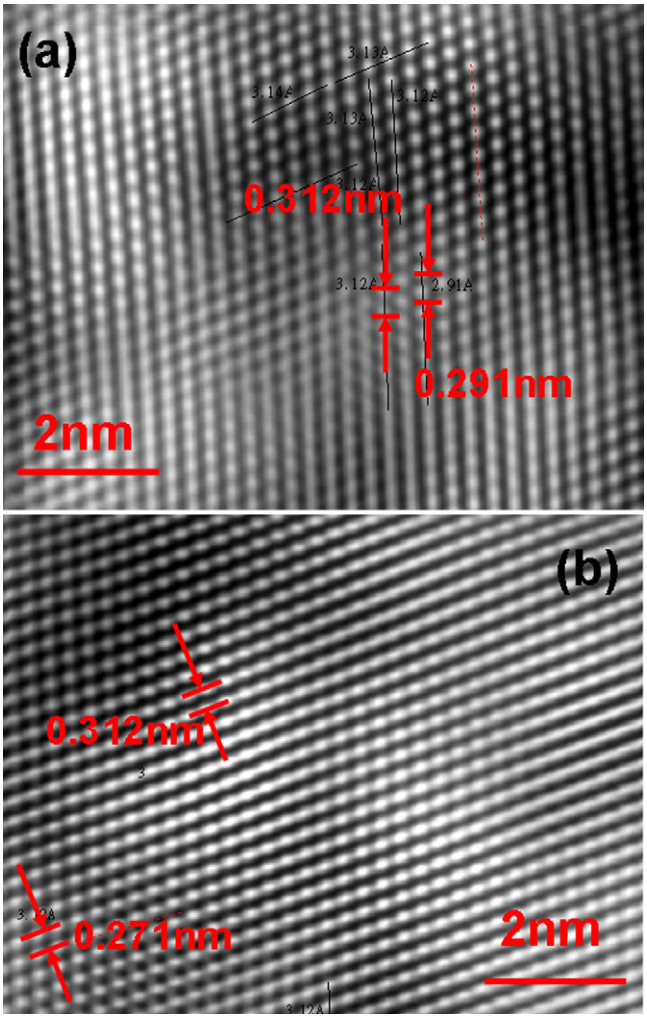

Fig. 7. HRTEM images of YSZ(111) for different oxygen pressures (a) $1\text{x}10^{-5}$ Torr (b) $5\text{x}10^{-4}$ Torr.

and 1×10^{-5} Torr-deposited YSZ thin films are 0.271 nm and 0.291 nm, respectively. Because the 0.271 nm and 0.291 nm are smaller than the perfect YSZ thin film of 0.312 nm, for that the measured lattice constant a is smaller than the real lattice constant a_0, as the results in Fig. 6 show.

4. Conclusions

The effects of oxygen pressures on structures of YSZ thin films deposited onto Si (100) substrate by E-beam evaporation are developed. At lower depositing pressure, the YSZ thin films are expitaxial on Si(100) substrate and the peak of plane (200) is the oriented crystallization and has the maximum texture coefficient. At higher chamber pressure, the YSZ thin films is expitaxial on surface SiO_{1-x} layer and the YSZ thin films will crystallize in according to the lowest surface energy orientation of plane (111). Although the surface energy of YSZ plane (111) is lower than those of planes (200) and (220), the lattice model shows that YSZ plane (200) is preferred orientation to grow on Si(100), which has been demonstrated in this study. The calculated a_o and a values are 0.51538–0.51567 nm and 0.51304–0.51503 nm, respectively, and the a_o value is smaller than the a value. However, the maximum lattice deviations for $1x10^{-3}$ Torr-deposited and $1x10^{-5}$ Torr-deposited YSZ thin films are 0.271 nm and 0.291 nm, respectively.

Acknowledgements

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