Effect of the Thickness of SiO₂ under Layer on the Initial Stage of Epitaxial Growth Process of Yttria-Stabilized Zirconia (YSZ) Thin Film Deposited on Si(001) Substrate

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Si(001)基板上へ成膜したイトリア安定化ジルコニア（YSZ）薄膜の初期の

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1. Introduction

Yttria-stabilized zirconia (YSZ) is one of most promising oxides that can be epitaxially grown on a Si(001) substrate. It is known that YSZ can suppress the inter-diffusion between Si and the film material. In addition, YSZ is an insulating material with a relatively high dielectric constant. Therefore YSZ thin films have been used most successfully as buffer layers for the deposition of superconductors such as YBa₂Cu₃O₇₋ₓ and ferroelectric materials such as PbTiO₃. The preparation of epitaxial YSZ thin films on a Si(001) substrate by several methods such as pulsed laser deposition (PLD), vacuum evaporation, ion-beam sputtering, and reactive sputtering has been reported. In the most of these reports, Si(001) after removal of the native SiO₂ by HF dipping was used as the substrate for deposition of epitaxial YSZ. However, it has also been reported that epitaxial YSZ can be obtained without removal of native SiO₂. Additionally it has been reported that a high-quality epitaxial YSZ thin film prepared by PLD and sputtering is obtained on a Si(001) substrate having native SiO₂ rather than on a Si(001) substrate after removal of native SiO₂. In the literature, the mechanism of epitaxial growth of YSZ thin film on a Si substrate containing SiO₂ has been reported to proceed according to the following Eqs. (1) or (2).

\[ \text{SiO}_2 + \text{Zr} \rightarrow \text{Si} + \text{ZrO}_2 \]  (1)

\[ 2\text{SiO}_2 + \text{Zr} \rightarrow \text{ZrO}_2 + 2\text{SiO} \]  (2)

In these equations, the reduction of SiO₂ is the key to grow epitaxial YSZ. However, the effect of the thickness of the SiO₂ layer on the epitaxial growth of YSZ has not been well investigated. In addition, there still remains the question as to how the epitaxial information from the substrate is transferred to the growing film via the SiO₂ layer. The purpose of this work is to approach the mechanism of epitaxial growth of YSZ on Si(001) as a function of the thickness of SiO₂.

2. Experimental

2.1 Film deposition

YSZ thin films were deposited by pulsed laser deposition (PLD) with a KrF excimer laser (\(\lambda=248\) nm) using YSZ (8 mol% \(\text{Y}_2\text{O}_3\)-stabilized \(\text{ZrO}_2\)) target. YSZ powder (Tosoh Corporation, Japan) was pressed into a pellet and sintered at 1500°C for 2 h in air to synthesize the YSZ target. The laser beam was focused by a quartz lens up to an energy density of about 2.0 J/cm² and at an angle of 45° on targets of YSZ which were rotated during the deposition. The substrates were heated up to 800°C at a heating rate of 20°C/min at 8.0 x 10⁻⁵ Pa O₂. After the temperature reached 800°C, YSZ was deposited in 8.0 x 10⁻⁵ or 7.3 x 10⁻² Pa O₂. The deposition rate of YSZ was 8 nm/min. Detailed growth conditions of YSZ are shown in Table 1.

2.2 Si substrate treatments

10 mm x 10 mm sized Si(001) substrates were cleaved from polished Si(001) wafers (n-type, 0.1-1.0 \(\Omega\) cm). The thickness of SiO₂ was determined by X-ray photoelectron spectroscopy (XPS) using monochromated Al Kα X-rays (1253.6 eV) at the takeoff angle of 30° (PSP450, PERKIN ELMER). The deposition conditions of YSZ are shown in Table 1.

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<th>Table 1. Deposition Conditions of YSZ Thin Film</th>
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angle of 45° under a pressure of less than 6.7 × 10⁻⁸ Pa. The total power applied to the Al Kα X-rays source was 300 W. The peaks were referenced to the C 1s peak at 284.6 eV for charge correction. The equation to determine the thickness \( t \) (nm) of SiO₂ was the following:

\[
t = \frac{\lambda}{\ln (1 + \frac{I_{sb}(\omega)}{I_{ox}(\omega)})} I_{sb} (\omega)
\]

where \( \lambda \) is the escape depth of Si 2p photoelectrons in the SiO₂ matrix (= 3.77 nm), \( I_{sb}(\omega) \) is the intensity of a clean Si substrate, \( I_{ox}(\omega) \) is that of a clean and thick SiO₂ substrate, and \( I_{sb} \) and \( I_{ox} \) are measured intensities of Si and SiO₂, respectively.²⁷

In this work, Si(001) substrates of various SiO₂ thicknesses were prepared as follows:

1. Si substrate having native SiO₂: This substrate was immediately cleaved and degreased with 2-propanol. The thickness of SiO₂ was 1.1 nm.

2. Si substrate after RCA cleaning:²⁸ This substrate was degreased with 2-propanol and cleaned according to the RCA method. The thickness of SiO₂ after RCA cleaning was 0.68 nm.

3. Hydrogen-terminated Si (H-terminated Si) substrate: The Si substrate after RCA cleaning was dipped in diluted HF (HF:H₂O = 1:10) to remove native SiO₂. For the Si substrate immediately after this treatment, no SiO₂ was detected by XPS. Therefore, the thickness of SiO₂ after HF dipping was 0.0 nm.

4. Thermally oxidized Si substrate (holding time at 800°C is 0 min): The substrate after HF dipping was heated to 800°C at the heating rate of 20°C/min in 8.0 × 10⁻⁵ Pa O₂. Immediately after the substrate temperature reached 800°C, the substrate was cooled to room temperature at the cooling rate of 20°C/min in 8.0 × 10⁻⁵ Pa O₂. The thickness after this treatment was 0.49 nm.

5. Thermally oxidized Si substrate (holding time at 800°C is 30 min): The H-terminated Si substrate was heated at 800°C for 30 min in 8.0 × 10⁻⁵ Pa O₂. The thickness after this treatment was 0.74 nm.

6. Si substrate having 1-μm-thick thermally oxidized SiO₂: This Si substrate was purchased from Shinetsu Handoutai, Japan. This substrate had a 1-μm-thick thermally oxidized SiO₂ layer. The substrate treatments are schematically shown in Fig. 1.

2.3 Characterization

The growth process was monitored in-situ using reflection high-energy electron diffraction (RHEED) operating at a 20 keV electron beam (RHD-300, Pascal). The development of elastic misfit strains in the YSZ during growth was measured by evaluating a series of RHEED patterns, an approach similar to that used by Whatley and Cohen²⁹ and Bardal et al.¹⁴

The lattice parameter and rocking curve measurements were carried out by a powder X-ray diffractometer (X’Pert-MPD (θ-θ), Philips) using Cu Kα radiation operating at 40 kV-40 mA. The thickness of the thin films was measured with a surface profile meter (Dektak3, Sloan, USA).

3. Results and discussion

Initially, the RHEED patterns of Si substrates before heating were measured at room temperature. Figures 2(a), (b), (c) and (d) correspond to the RHEED patterns observed along the <100> azimuths of Si(001) having 0, 0.74, 1.1-nm and 1-μm-thick SiO₂ layers, respectively. Figures 2(a)–(d) indicate that sharp streaks, Kikuchi bands as well as Kikuchi lines, were observed for the Si substrate having a less than 1.1-nm-thick SiO₂ layer, on the other hand, no specific RHEED pattern was observed for the Si substrate having a 1-μm-thick SiO₂ layer.

At first, the Si substrate having a 0.49-nm-thick SiO₂ layer (hereafter denoted as SiO₂ (0.49 nm)/Si) was selected, and thickness dependency of YSZ thin films on the crystal structure was observed. Figure 3 shows the change of the in-situ RHEED pattern with the thickness of YSZ deposited at 800°C in 7.3 × 10⁻² Pa O₂. The thickness of YSZ for Figs. 3(a), (b), (c), (d) and (e) is 0, 0.8, 1.6, 5 and 20 nm, respectively. These figures indicate that the sharp RHEED pattern for SiO₂ (0.49 nm)/Si (Fig. 3(a)) disappears completely by the deposition of 0.8-nm-thick YSZ (Fig. 3(b)), and a streak of YSZ is observed if the thickness of YSZ is more than 1.6 nm (Figs. 3(c)–(e)). The change of the RHEED pattern with the thickness of YSZ was also quantitatively analyzed from the viewpoint of the in-plane lattice parameter of YSZ. Figure 4 shows the change of the in-plane lattice parameter of YSZ with the thickness of YSZ. In Fig. 4, open and closed
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Circles denote data deposited in 8.0 × 10⁻⁵ and 7.3 × 10⁻² Pa O₂, respectively. For both deposition pressures, epitaxial growth of YSZ was achieved on Si(001) with a cube-on-cube relationship. In Fig. 4, data reported by Bardal et al. are also shown. Comparing their data with ours, it is apparent that these data agree well. Next the experiments were carried out on Si substrates having SiO₂ layers of thicknesses. Figure 5 shows the change of in-plane lattice parameter of YSZ with YSZ deposited on Si having 0.68-, 0.74- and 1.1-nm-thick SiO₂ layers deposited in 8.0 × 10⁻⁵ Pa O₂. In this case, the YSZ films were also epitaxially grown on the Si (001) substrate. This experiment was also carried out on Si having a 1-nm-thick SiO₂ layer, however, the film was not epitaxial but polycrystalline. As shown in Fig. 5, it is surprising that the in-plane lattice parameter was independent of the thickness of YSZ. Although there have been many reports on the preparation of epitaxial YSZ thin films on Si (001) substrates, the result shown in Fig. 5 has not been reported. Comparing the result shown in Fig. 5 with that in Fig. 4, it is noted that the thickness of SiO₂ determines the strain in the thin film at the initial stage of deposition.

The result shown in Fig. 4 indicates that tensile stress due to the lattice mismatch between YSZ and the Si substrate (≈ 5.0%) is applied to the YSZ thin film at the initial stage of YSZ deposition if the thickness of the SiO₂ film is 0.49 nm. This finding suggests that the SiO₂ layer on the Si (001) surface was completely reduced by the deposition of YSZ at the initial stage. The species generated by the laser ablation from the YSZ target is uncertain; however, it is inferred to be metal Zr or a reduced zirconium oxide such as ZrOₓ which would arrive at the SiO₂ layer to cause a reduction reaction such as that shown by Eqs. (1) or (2). Figure 4 also indicates that the stress due to the lattice mismatch is significantly released if the thickness of YSZ is over 5 nm. The reason for this is due to the generation of misfit dislocations and/or regrowth of amorphous SiO₂ at the YSZ/Si interface owing to oxygen in-diffusion through the YSZ layer during the latter stages of growth. The inferred mechanism to explain the result shown in Fig. 4 is shown in Fig. 6.
On the contrary, if the thickness of the SiO$_2$ layer is 0.68, 0.74 or 1.1 nm, the change of the in-plane lattice parameter with the thickness of YSZ is constant as shown in Fig. 5. It should be noted that these YSZ films are also epitaxially grown on SiO$_2$/Si substrates. As mentioned above, the reduction of SiO$_2$ is believed to proceed on the deposition of the YSZ thin film. However, if the entire SiO$_2$ layer is reduced irrespective of the thickness of SiO$_2$ (between 0.49 and 1.1 nm), the change of the in-plane lattice parameter with the thickness of YSZ should show the same tendency. Therefore, the results shown in Figs. 4 and 5 suggest that the mechanism of epitaxial growth of YSZ differs depending on the thickness of SiO$_2$. If the thickness of SiO$_2$ is between 0.68 and 1.1 nm, the reduction of SiO$_2$ occurs, however, not all of SiO$_2$ is reduced and a thin SiO$_2$ layer remains on the Si surface. In this case, the YSZ thin film is considered to deposit on SiO$_2$. The structure of the SiO$_2$/Si interface has been extensively investigated. According to these reports, there exists a thin crystalline phase of SiO$_2$ at the interface between amorphous SiO$_2$ and the Si (001) surface as a crystalline transition layer. From X-ray scattering data, it was inferred that the crystalline SiO$_2$ at the interface is tridymite or cristobalite. By TEM lattice image observation, Ourmazd et al. reported that the crystalline SiO$_2$ is tridymite and its thickness is around 0.5 nm. On the other hand, Hane et al. applied first-principles total-energy and force calculations and concluded that the crystalline SiO$_2$ on Si(001) is $\beta$-cristobalite on the first and second layers from the interface. Recently, this calculated result was confirmed by direct TEM observation. It should be noted that the atomic configuration of $\beta$-cristobalite is very close to that of Si, therefore, an epitaxial relation between $\beta$-cristobalite and Si(001) is realized as shown by the model in Fig. 7, which model was proposed by Watanabe and Ohdomari. Based on these reports, the result shown in Fig. 5 can be considered to be that the reduction of SiO$_2$ by the deposition of YSZ also occurs; however, not the entire SiO$_2$ is reduced. Crystalline SiO$_2$ ($\beta$-cristobalite) remains, and on the crystalline SiO$_2$ transition layer, YSZ is epitaxially grown. Therefore, in this case, epitaxial information of the Si substrate is transferred to YSZ via SiO$_2$. The mechanism of the change of in-plane lattice parameter with the thickness of YSZ (thickness of SiO$_2$ is between 0.68 and 1.1 nm) is schematically shown in Fig. 8. As mentioned above, on the Si substrate having a 1-μm-thick SiO$_2$ layer, epitaxial growth of YSZ is not realized. This supports the finding that the crystalline SiO$_2$ exists only on the interface of Si.

Finally, the change of FWHM of the rocking curve with the thickness of SiO$_2$ for 20-nm-thick YSZ(002) deposited in 8.0 $\times$ 10$^{-5}$ and 7.3 $\times$ 10$^{-2}$ Pa O$_2$ is shown in Fig. 9. This figure illustrates that the minimum FWHM value was obtained when the thickness of SiO$_2$ was 0.68 nm. This indicates that the Si substrate after removal of native SiO$_2$ is not suitable for the epitaxial growth of YSZ and a Si substrate having an approximately 0.7-nm-thick SiO$_2$ layer is suitable. This suggests that the 0.7-nm-thick SiO$_2$ layer is reduced by the deposition of YSZ, and the thickness of the remaining SiO$_2$ is close to the thickness of the crystalline SiO$_2$ layer having a $\beta$-cristobalite structure.

### 4. Conclusions

It is well known that yttria-stabilized zirconia (YSZ) is epitaxially grown on a Si(001) substrate. However, the mechanism of an epitaxial growth has not been clarified yet. In this work, the epitaxial growth process of a YSZ thin film on Si(001) substrates having thicknesses of various SiO$_2$ layers was in-situ monitored by reflection high-energy electron diffraction (RHEED). If the thickness of SiO$_2$ was 0.49 nm, the in-plane lattice parameter of YSZ at the initial stage of deposition (the thickness of YSZ was below 5 nm), was very close to that of the Si substrate. The in-plane lattice parameter of YSZ significantly decreased approaching that of bulk YSZ when the thickness of YSZ was over 5 nm. On the contrary, when the thickness of SiO$_2$ was between 0.68
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and 1.1 nm, the in-plane lattice parameter did not change with the thickness of YSZ. The reason for the change of this lattice relaxation with the thickness of SiO₂ can be ascribed to the reduction reaction of amorphous SiO₂ and the structure of SiO₂ being ß-cristobalite at the interface of amorphous SiO₂ and the Si substrate.

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References