Preparation of Epitaxial YSZ Thin Film Deposited on SiO2/Si(001) at Room Temperature by Pulsed Laser Deposition (PLD)

Hirokazu ISIGAKI, Tomoaki YAMADA, Naoki WAKIYA, Kazuo SINOZAKI and Nobuyasu MIZUTANI

Department of Metallurgy and Ceramic Science, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152–8550

PLD 法による SiO2/Si(001) 基板上エピタキシャル YSZ 薄膜の室温合成

石垣寛和・山田智明・脇谷尚樹・篠崎和夫・水谷惟恭

東京工業大学大学理工学研究科材料工学科 152–8550 東京都目黒区大岡山 2–12–1

YSZ thin films were deposited by pulsed laser deposition (PLD) on Si(001) with native SiO2. H-terminated Si(001) and ablated Si on H-terminated Si(001) at various temperatures (800, 600, 400, 200°C and RT (room temperature)). The crystallinity of YSZ thin film on Si(001) with native oxide was the highest among the three substrates. YSZ thin film on ablated Si on H-terminated Si(001) was amorphous. We suggest that an ultrathin SiO2 layer (<1.1 nm) is necessary for crystal growth of YSZ thin film. A two-step process was attempted to prepare epitaxial YSZ thin films. First, YSZ thin films were deposited on Si(001) with native SiO2 at 800°C in 8.0 × 10⁻¹⁻⁻² Pa O2 (reduction condition). Second, YSZ thin films were deposited on Si(001) with native SiO2 at various temperatures (800, 600, 400, 200°C and RT) in 7.3 × 10⁻¹⁻⁻² Pa O2. All YSZ thin films deposited by a two-step process were epitaxial. The reason for this mechanism is discussed.

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1. Introduction

Yttria-stabilized zirconia (YSZ) is one of the most promising oxides that can be epitaxially grown on Si(001) substrate.1,2) 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 (εr = 27).3) Therefore, YSZ thin films have been used most successfully as buffer layers for the deposition of superconductors such as YBa2Cu3O7-x5)-8) and ferroelectric materials such as PbTiO3.9) The preparation of epitaxial YSZ thin films on Si(001) substrate by several methods such as pulsed laser deposition (PLD),10),11) vacuum evaporation,12) electron beam evaporation13)-16) and ion beam sputtering,17)-20) has also been reported. In the most of these reports, Si(001) after removal of the native oxide by HF dipping was used as the substrate for deposition of epitaxial YSZ thin film. However, it has also reported that epitaxial YSZ thin film can be obtained without the removal of native SiO2.21) Additionally, it has been reported that a high-quality epitaxial YSZ thin film prepared by PLD and sputtering is obtained on Si(001) substrate having native SiO2 compared to that on a Si(001) substrate after removal of native SiO2.22) In the literature, the mechanism of epitaxial YSZ thin film formation on Si(001) substrate with SiO2 has been reported to proceed according to Eqs. (1) or (2).23)-26)

\[
\begin{align*}
\text{SiO}_2 + \text{Zr} &\rightarrow \text{Si} + \text{ZrO}_2 \quad (1) \\
2\text{SiO}_2 + \text{Zr} &\rightarrow \text{ZrO}_2 + 2\text{SiO} \quad \text{(volatile)} \quad (2)
\end{align*}
\]

In these equations, the reduction of SiO2 is the key to growing epitaxial YSZ thin film. The effect of thickness of SiO2 on the crystal quality of YSZ thin films at 800°C has been reported.25) However, epitaxial YSZ thin films deposited at various temperatures have not been reported. We tried to prepare epitaxial YSZ thin films deposited at various temperatures (800, 600, 400, 200°C and RT (room temperature)). The purpose of this work is to determine the mechanism of YSZ thin film formation at various temperatures and to prepare epitaxial YSZ thin film under such conditions.

2. Experimental

2.1 Film deposition

YSZ thin films were deposited by PLD with KrF excimer laser (λ = 248 nm) using YSZ (8 mol% Y2O3-stabilized ZrO2) as target. YSZ powder (Tosoh Corporation) was pressed into a pellet and sintered at 1500°C for 2 h in air to synthesize YSZ target. The laser beam was focused by a quartz lens up to an energy density of about 2.0 J/cm² and an angle of 45° on YSZ target which was rotated during deposition. The substrates were heated to 800°C at a rate of 20°C/min at 8.0 × 10⁻¹⁻⁻² Pa O2. After the temperature reached 800°C, YSZ was deposited at 8.0 × 10⁻¹⁻⁻² or 7.3 × 10⁻¹⁻⁻² Pa O2. The deposition rate of YSZ was 8 nm/min. The detailed growth conditions of YSZ are shown in Table 1.

2.2 Si substrate treatment

Si substrates (10 mm × 10 mm) were cut from polished Si (001) wafers (n-type, 0.1–10 ncm). In this work, two treatment methods were applied to Si(001) substrates. One method involved only the use of 2-propanol in order to degrease the residual organics. The Si(001) substrate having native SiO2 layer was treated by this method. The thickness of the native SiO2 layer was determined to be 1.13 nm by X-ray photoelectron spectroscopy (XPS) (PHI5500, PERKIN-ELMER) using monochromated Al Kα X-rays at the takeoff angle of 45° under a pressure of less than 6.8 × 10⁻¹⁻⁻⁸ Pa. The total power applied to the Al Kα X-rays source was 300 W. The peaks were referenced to the C1s peak at 284.6 eV for charge corrections. The equation to determine the thickness t (nm) of SiO2 is as follows:

\[ t = \lambda \cdot \ln \left( 1 + \frac{I_{sh}(\infty)}{I_{ax}(\infty)} \right) \cdot \frac{I_{ax}}{I_{sh}} \quad (3) \]

where λ is the escape depth of Si 2p photoelectrons in the matrix (≈ 3.77 nm), I_{sh}(∞) is the intensity of a clean Si substrate, I_{ax}(∞) is that of a clean and thick SiO2 substrate and I_{sh} and I_{ax} are measured intensities of Si and SiO2, respectively.26)
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Table 1. Deposition Conditions for YSZ Thin Films

<table>
<thead>
<tr>
<th>Laser</th>
<th>KrF excimer laser (λ = 248 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>YSZ (BY)</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>55 mm</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>7 Hz</td>
</tr>
<tr>
<td>Spot size</td>
<td>0.1 cm²</td>
</tr>
<tr>
<td>Laser energy density</td>
<td>1.0 J/cm²</td>
</tr>
<tr>
<td>YSZ thickness</td>
<td>100 nm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>800, 600, 400, 200, 27 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>8.0 x 10⁻⁶, 7.3 x 10⁻² Pa O₂</td>
</tr>
</tbody>
</table>

Fig. 1. RHEED patterns of Si(001) substrate at room temperature. (a), (b), (c) and (d) correspond to Si(001) substrates having <0.49-, 0.49-, 1.1-nm, and ablated Si, respectively.

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

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

2. Hydrogen-terminated Si (H-terminated Si) substrate: This substrate after 2-propanol cleaning was dipped in diluted HF (HF: H₂O = 1:10) to remove native SiO₂. Immediately after this treatment, no SiO₂ was detected on the substrate by XPS. Therefore, the thickness of SiO₂ after HF dipping was 0.0 nm.

3. Thermally oxidized Si substrate (holding time at 400°C in 8.0 x 10⁻⁵ Pa O₂ is 0 min): The substrate after HF dipping was heated to 400°C at a rate of 20°C/min in 8.0 x 10⁻⁵ Pa O₂. Immediately thereafter, the substrate was cooled to room temperature at a rate of 20°C/min in 8.0 x 10⁻⁵ Pa O₂. The thickness after this treatment was <0.49 nm.

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

5. Ablated Si on H-terminated Si: This substrate was prepared using Si substrate as target by PLD. Si was ablated immediately before the deposition of YSZ thin films at various temperatures (800, 600, 400, 200°C and RT).

2.3 Characterization

The structural properties of the films were characterized by X-ray diffraction (XRD) using Cu Kα radiation operating at 40 kV-45 mA (X'Pert-MPD (Į-Į, Open Eulerian Cradle), Phillips) and reflection high energy electron diffraction (RHEED) with 20 kV electron beam (RHD-300, Pascal) introduced along the <100> azimuth of the Si(001) substrate. Film thickness measurement was achieved by means of using the surface profile method (Dektak3, Sloan).

3. Result and discussion

Initially, the RHEED patterns before heating were observed at room temperature. Figures 1 (a), (b), (c), and (d) correspond to the RHEED patterns observed along the <100> azimuths of Si(001) having 0, 0.49, 1.1 nm-thick SiO₂, and ablated Si, respectively. Sharp streaks, Kikuchi bands as well as Kikuchi lines, were observed for the Si substrates in Fig. 1(a).

Figure 2 shows XRD patterns of YSZ deposited on Si (001) substrates in Figs. 1 (a), (c) and (d) at 800°C in 7.3 x 10⁻² Pa O₂. It is found that YSZ thin films deposited on substrates shown in Figs. 1 (a) and (c) were epitaxial, and that deposited on the substrate shown in Fig. 1 (d) was amorphous. Figure 3 shows XRD patterns of YSZ deposited on Si (001) substrates shown in Figs. 1 (a), (c) and (d) at 400°C.
It is found that YSZ thin film deposited on the substrate shown in Fig. 1(c) was epitaxial, and those deposited on the substrates shown in Figs. 1(b) and (d) were amorphous. Figures 2 and 3 indicate that an ultrathin SiO2 layer (<1.1 nm) was necessary for the crystallization of YSZ film.

Figure 4 shows XRD patterns of YSZ deposited on Si (001) with native SiO2 at various temperatures (800°C, 600°C, 400°C, and 200°C) in 7.3 x 10^{-2} Pa O2. The YSZ thin film deposited at 800°C was epitaxial. The YSZ thin films deposited at 600°C and 400°C had preferred <111> orientation. The YSZ thin film deposited at 200°C was amorphous.

In order to prepare epitaxial YSZ thin film on Si (001) substrate, a SiO2 layer is necessary. In the case of using Si (001) with SiO2, the peak of the XRD pattern of YSZ thin film was very sharp (Fig. 2). Therefore, we selected Si (001) with native SiO2 as the substrate. We tried to deposit epitaxial YSZ thin film at low temperature on Si (001) with native SiO2 by the following process. First, this substrate after 2-propanol treatment was heated to 800°C at a rate of 20°C/min in 8.0 x 10^{-5} Pa O2. Then, YSZ thin film of 0.8 nm thickness was deposited at 800°C in 8.0 x 10^{-5} Pa O2 (reduction condition). Epitaxial growth of YSZ thin film was monitored using in-situ RHEED. Second, this YSZ thin film was cooled to various temperatures (800°C, 600°C, 400°C, and 200°C) at a rate of 20°C/min in 8.0 x 10^{-5} Pa O2. Then, YSZ thin film of 0.8 nm thickness was deposited at 800°C in 8.0 x 10^{-5} Pa O2 (reduction condition). Finally, this film was cooled at a rate of 20°C/min in 8.0 x 10^{-5} Pa O2. Figure 5 shows the schematic of the deposition process.

Figure 6 shows XRD patterns of YSZ deposited on epitaxial YSZ thin film (0.8 nm)/Si (001) with native SiO2 at various temperatures (800°C, 600°C, 400°C, and 200°C) in 7.3 x 10^{-2} Pa O2. The thickness of YSZ thin film was 100 nm. It is noted that all YSZ thin films were epitaxially grown. These results also indicate that the initial layer is important for epitaxial growth.

The change of FWHM of the rocking curve for 100-nm-

SiO2 was reduced.

SiO2

HZS

Si

Deposited at 800°C
Deposited at 600°C
Deposited at 400°C
Deposited at 200°C
Deposited at room temperature

Fig. 5. Schematic of deposition process.
epitaxially grown on Si(001) substrate at 800°C. However, the effect of the SiO₂ layer on epitaxial growth and polycrystal growth of YSZ thin film deposited on Si(001) substrate was not clear. We found that an ultrathin SiO₂ layer (<1.1 nm) was necessary for epitaxial growth. We also found that the crystallinity of YSZ thin film deposited on Si(001) substrate at low temperature to suppress the growth of SiO₂ layer. We used a two-step process to prepare epitaxial YSZ thin films. First, YSZ thin films were deposited on Si(001) with native SiO₂ at 800°C in 8.0 × 10⁻⁵ Pa O₂ (reduction condition). Second, YSZ thin films were deposited on Si(001) with native SiO₂ at various temperatures (800, 600, 400, 200°C and RT (room temperature)) in 7.3 × 10⁻² Pa O₂. All YSZ thin films deposited by the two-step process were epitaxial. Dielectric constant increased with increasing deposition temperature, suggesting that the growth of SiO₂ layer was suppressed at low temperature.

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