Effect of deposition conditions and buffer layers on amorphous or polytype phase formation in Al$_2$O$_3$ thin films by chemical vapor deposition using tri-methyl aluminum

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Al$_2$O$_3$ thin films were deposited on (001)Si substrate through Cr$_2$O$_3$/yttria-stabilized-zirconia (YSZ) buffer layer by cold-wall type chemical vapor deposition method with tri-methyl aluminum as a raw material. By changing the deposition temperature, different polytypes of Al$_2$O$_3$ thin films were formed. At lower temperatures (1123–1173 K), $\eta$-Al$_2$O$_3$ and amorphous Al$_2$O$_3$ were found in mixture. With increasing the deposition temperature, the series of Al$_2$O$_3$ polytypes ($\gamma$, $\kappa$ and $\alpha$) appeared in the order of decreasing the unit cell volume per Al atom. At 1323 K, single-phase $\alpha$-Al$_2$O$_3$ thin film was obtained in success. On (001)Cr$_2$O$_3$/YSZ/Si substrate, epitaxial (00)$\alpha$-Al$_2$O$_3$ thin-film was grown, however, on (001)YSZ/Si substrate, epitaxial (00)$\alpha$-Al$_2$O$_3$ thin film was formed. It shows that buffer layer also has much influence on polytype of Al$_2$O$_3$ thin film. On the other hand, there exist the polycrystalline $\alpha$-Al$_2$O$_3$ and Cr$_2$O$_3$ have the same Miller index ($h$ $k$ $l$), therefore, polycrystalline $\alpha$-Al$_2$O$_3$ thin film was deposited on the polycrystalline Cr$_2$O$_3$ buffer layer in which each Al$_2$O$_3$ and Cr$_2$O$_3$ grain has an epitaxial relation. This epitaxial growth can be explained by both the similarity in crystal structure between Al$_2$O$_3$ film and Cr$_2$O$_3$ buffer layer, and also their moderate lattice mismatch.

Key-words : CVD, Thin film, Buffer layer, Alumina, Polytype, Epitaxial growth

1. Introduction

Among the various polytypes of Al$_2$O$_3$ such as $\alpha$, $\kappa$, $\gamma$, $\eta$, $\delta$, and $\chi$ phases, $\alpha$ phase is only stable and the others are metastable with higher Gibbs formation energies. $\eta$-Al$_2$O$_3$ and stable $\kappa$-Al$_2$O$_3$ are used because of their high hardness and heat resistance. To make these Al$_2$O$_3$ coatings in industry, chemical vapor deposition (CVD) is applied due to excellent step coverage and large deposition area. In CVD process, choosing the aluminum source material and controlling its gaseous phase oxidation are important.

For aluminum source materials, there were a lot of materials tested such as aluminum tri-isopropoxide, aluminum chloride (AlCl$_3$), aluminum acetylaceton [Al(acac)$_3$] and tri-methyl aluminum (TMA, Al(CH$_3$)$_3$). AlCl$_3$ have been used for $\alpha$-Al$_2$O$_3$ thin film with CO$_2$–H$_2$ by thermal CVD in cutting tools industry since the 1970s. In this process, H$_2$ reacts with CO$_2$ to create a low-oxygen partial-pressure atmosphere and to prevent rapid oxidation of AlCl$_3$ in gaseous phase. However, the obtained Al$_2$O$_3$ thin films deposited at lower temperatures tend to include chlorine residue. Recently, much attention has been paid to TMA [Al(CH$_3$)$_3$] as aluminum source. By atomic layer deposition (ALD), dense and amorphous Al$_2$O$_3$ thin-films can be obtained. By plasma-enhanced CVD, $\gamma$-Al$_2$O$_3$ thin films were deposited with N$_2$O as an oxidizing agent on Si substrate. By thermal CVD, $\gamma$-Al$_2$O$_3$ thin films were also deposited with O$_2$ on GaN. However, no report describes $\alpha$-Al$_2$O$_3$ thin film deposition on Si substrate with TMA as a raw material.

To fabricate the crystalline thin film in CVD or PVD process, buffer layer technique has a great potential. Actually, Cr$_2$O$_3$ thin films (corundum structure) were grown epitaxially on yttria-stabilized-zirconia (YSZ) buffer (001)Si substrate using pulsed laser deposition (PLD) method. Similarly, by sputtering method, polycrystalline $\alpha$-Al$_2$O$_3$ thin film was deposited on polycrystalline Cr$_2$O$_3$-buffered Si substrate in which each Al$_2$O$_3$
and Cr$_2$O$_3$ grains have an epitaxial relation. No report, however, has described α-Al$_2$O$_3$ thin film deposited on Cr$_2$O$_3$/YSZ/Si substrate using CVD so far. If α-Al$_2$O$_3$ thin film is deposited on a Cr$_2$O$_3$-buffered Si substrate by CVD method, it must be useful information for next-generation cutting tool coating.

In this study, Al$_2$O$_3$ thin films formation was investigated with a horizontal cold-wall type thermal CVD using TMA as a raw material, by flowing O$_2$ for oxidation gas and Ar on a buffered (001)Si substrate. Discussion was made on how the Al$_2$O$_3$ polycrystalline was changed depending on the deposition temperature and the buffer layer structure.

2. Experimental

In this study, single crystal Si was used as the substrate. Buffer layers were deposited on (001) plane of Si using PLD. Four types buffered substrates were YSZ/Si, Cr$_2$O$_3$/YSZ/Si, P-Cr$_2$O$_3$/Y-YSZ/Si, and P-Cr$_2$O$_3$/P-YSZ/Si, where P- denotes the polycrystalline. The P-YSZ was formed by the following process. After the amorphous YSZ film was deposited on Si substrate at room temperature (298 ± 5 K) using PLD, then annealed at 1373 K for 1.8 × 10$^4$s. The other buffer layers were also deposited by PLD using a KrF excimer laser ($\lambda = 248$ nm) at the substrate temperature of 1023 K in vacuum with oxygen partial pressure of 7.33 × 10$^{-2}$ Pa. The laser fluence and the repetition rate were approximately 1.2 J cm$^{-2}$ and 7 Hz, respectively. The YSZ, Cr$_2$O$_3$, and CeO$_2$ targets for PLD were fabricated by solid-state sintering. That is, YSZ (8 at%Y$_2$O$_3$–92 at%ZrO$_2$), Cr$_2$O$_3$, and CeO$_2$ powders were compacted into pellets of 20 mm in diameter and 5 mm in thickness. The pellets were sintered at 1723 K for 1.08 × 10$^5$s, at 1573 K for 2.16 × 10$^4$s, and at 1573 K for 5.4 × 10$^4$s. In addition to the buffered Si substrates above, a Cr$_2$O$_3$ sintered body was used as the substrate.

On these substrates, Al$_2$O$_3$ thin films were deposited by using the low-pressure, horizontal, cold-wall type thermal CVD. Figure 1 shows a schematic diagram of this process. TMA was purchased from a company (Tri Chemical Lab. Inc., Japan). TMA was introduced into the CVD chamber without carrier gas. The flow rate of TMA vapor was adjusted by a needle valve. After the substrate was set on Inconel susceptor (50 mmφ × 31 mm, Inconel 601), it was heated by induction heating (RF-5KN4, 20–50 kHz, 5 kW; NEC Tokin Corp., Japan). Table 1 summarizes the CVD deposition parameters. For the temperature calibration, actual substrate temperatures were measured using a K-type thermocouple attached on the upper surface of Si substrate with 10 × 10 × 0.5 mm$^3$ with Al$_2$O$_3$-based cement paste (Aron Ceramics; Toagosei Chemical Industry Co. Ltd., Japan).

The film thickness was measured with a surface profilometer (Dektak$^3$; Sloan Technology Corp., USA). The phases and crystallinity of the deposited films were evaluated using X-ray diffractometer (XRD, MPD; Malvern PANalytical, Netherland) with CuK$_\alpha$ radiation. Crystal orientation and reciprocal-space-mapping measurements were done with thin film XRD (MRD; Malvern PANalytical, Netherland) to analyze the epitaxial relations between the film and the buffer layer.

3. Results and discussion

The effect of deposition (substrate) temperature on Al$_2$O$_3$ polycrystalline is shown in Figure 2. This is the case of Cr$_2$O$_3$/YSZ/Si substrate (both Cr$_2$O$_3$ and YSZ buffer layer were 30 nm in thickness). In Fig. 2(a), good lattice matching can be seen between (001)YSZ and (001)Si, and also (001)Cr$_2$O$_3$ and (001)YSZ. The former epitaxial growth is well-known to us. The latter epitaxial growth has a twin domain in the c-axis direction. Figures 2(b)–2(f) show the change in Al$_2$O$_3$ polycrystalline depending on the deposition temperatures. At 1123 and 1173 K, η-Al$_2$O$_3$ are detected. The mixed phases of κ- and γ-Al$_2$O$_3$ are detected at 1223 K. κ, γ, and α-Al$_2$O$_3$ are detected at 1273 K. Only α-Al$_2$O$_3$ is observed at 1323 K. It reveals that single-phase α-Al$_2$O$_3$ thin-film can be obtained by thermal CVD with TMA.

Figure 3 shows the relation between the deposition rate of Al$_2$O$_3$ thin films and the deposition temperature. Since TMA tends to react with oxygen rapidly and forms oxide particles by gas-phase homogeneous nucleation, decomposition of TMA increases with increasing the deposition temperature. Simultaneously, the CVD reaction at the sub-

![Figure 1: Schematic diagram of cold-wall type thermal CVD.](Image)

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**Table 1.** Deposition conditions for Al$_2$O$_3$ thin film by cold-wall type thermal CVD process

| Deposition Temperature | Chamber Pressure | TMA Vaporizer Temperature | Flow Rate of TMA | Flow Rate of O$_2$ Gas | Flow Rate of Ar Gas | Flow Rate of O$_2$ Gas | Flow Rate of Ar Gas | Deposition Time |
|------------------------|-----------------|---------------------------|-----------------|------------------------|-------------------|------------------------|-------------------|-----------------|
| 1123–1323 K            | 133.32 Pa       | 303 K                     | 3.3 × 10$^{-6}$-5.0 × 10$^{-9}$ m$^3$s$^{-1}$ | 1.26 × 10$^{-6}$ m$^3$s$^{-1}$ | 1.26 × 10$^{-6}$ m$^3$s$^{-1}$ | 3.6 × 10$^3$ s |
strate surface is enhanced with increasing the temperature. As shown in Fig. 3, the deposition rate rises gradually between 1123 and 1173 K, because the gas phase oxidation and homogeneous nucleation are moderate and because the amount of TMA supply for CVD process is close to constant at the lower temperature range. From 1173 to 1223 K, the gas-phase homogeneous nucleation is slightly enhanced. Then the amount of TMA is reduced, however, CVD reaction on the substrate is enhanced, causing that the deposition rate increased. From 1223 to 1323 K, the amount of TMA decreases dramatically because the gas-phase homogeneous nucleation occurs rapidly. Based on the discussion above, the change in Al₂O₃ deposition rate as a function of the deposition temperature has a maximum as shown in Fig. 3.

It is well known that amorphous Al₂O₃ decreased the strength of Al₂O₃-coated cutting tools. Therefore, the Al₂O₃ film is needed in industry containing higher amounts

![Fig. 2. XRD patterns of (a) Cr₂O₃/YSZ-buffered Si substrate and (b)−(f) Al₂O₃ thin films prepared on Cr₂O₃/YSZ/Si with 1123–1323 K deposition temperature. Substrate: Cr₂O₃/YSZ/Si, TMA flow rate: 3.3 × 10⁻⁹ m³ s⁻¹, Other deposition conditions: shown in Table 1.](image)

![Fig. 3. Effects of deposition temperature on deposition rate of Al₂O₃ thin film deposited on Cr₂O₃/YSZ/Si substrate by CVD. Substrate: Cr₂O₃/YSZ/Si, TMA flow rate: 3.3 × 10⁻⁹ m³ s⁻¹, Other deposition conditions: shown in Table 1.](image)
of crystalline Al₂O₃ polytypes, especially $\alpha$ or $\kappa$-Al₂O₃. To make clear how much Al₂O₃ polytypes are in the thin film of this study, semi-quantitative estimation of the amount of each Al₂O₃ polytype per unit volume of Al₂O₃ thin film was carried out. At first, the amount of each crystalline Al₂O₃ polytype was evaluated using the structure factor ($F$) with Rietvelt software (X-Pert HighScore plus software, ver. 4.7; PANalytical). The total amount of crystalline phase was obtained by using intensity and the $F$ values for all detected polytypes and comparing the amounts of amorphous Al₂O₃ phase in Al₂O₃ films.

For XRD measurements, the accelerating voltage and the current were fixed at 40 kV and 30 mA, respectively. The X-ray irradiation area at diffraction angles of $\alpha$(0012), $\kappa$(006), $\gamma$(333), and $\eta$(333) were adjusted at almost equal. The integrated intensity of XRD peaks per unit volume was calculated from the intensity in Fig. 2 and the thickness in Fig. 3. The Inorganic Crystal Structure Database was referred for the Al and O atom positions for each polytype. The measured XRD peak intensity is proportional to $F^2$. The multiplicity factor is regarded as unity because of the epitaxial thin film. The volume fraction of $\alpha$-Al₂O₃ in unit volume of thin film must be proportional to $I_{\alpha(hkl)} / (t \cdot |F_{\alpha(hkl)}|^2)$, where $I_{\alpha(hkl)}$ denotes the observed integrated intensity for $(h k l)$ reflection, $t$ expresses the film thickness, and $F_{\alpha(hkl)}$ stands for the structure factor for $(h k l)$ reflection. The summation of each Al₂O₃-polytype fraction in the unit volume of the Al₂O₃ thin film can be described as shown below.

$$\sum \frac{I_{\alpha(0012)} + I_{\kappa(006)} + I_{\gamma(333)} + I_{\eta(333)}}{t \cdot |F_{\alpha(0012)}|^2 + |F_{\kappa(006)}|^2 + |F_{\gamma(333)}|^2 + |F_{\eta(333)}|^2}$$

Figure 4 shows the effect of the deposition temperature on the volume fraction of each Al₂O₃ polytype in the unit volume of thin film. The total amount of crystalline Al₂O₃ polytypes are also shown in the figure. From Fig. 4(a), it is seen that the total amount of crystalline Al₂O₃ polytypes increases with increasing the deposition temperature, and it is almost the same as the $\alpha$-Al₂O₃ fraction. Figure 4(b) shows an enlargement of Fig. 4(a) at the lower volume fraction. At 1123 to 1173 K, the $\eta$-Al₂O₃ polytype is the dominant crystallized phase of the film. The $\kappa$-Al₂O₃ and $\gamma$-Al₂O₃ are formed at 1223 K. However, $\alpha$-Al₂O₃ is the main fraction together with a small amount of $\kappa$-Al₂O₃ and $\gamma$-Al₂O₃ at 1273 K. Finally, a large amount of $\alpha$-Al₂O₃ polytype is obtained at 1323 K.

On the other hand, we can estimate the amount of amorphous phase in each deposition temperature semi-quantitatively from Fig. 4. This estimation also shows the small amount of $\eta$-phase and the large amount of amorphous phase were deposited at lower deposition temperatures (1123 and 1173 K). Similarly, small amounts of $\kappa$-phase and large amounts of amorphous phase were deposited at intermediate deposition temperature (1223 K). At higher deposition temperatures (1273 and 1323 K), larger
amounts of $\alpha$-Al$_2$O$_3$ were deposited on the Cr$_2$O$_3$/YSZ/Si substrate. These results agree well to Fig. 2. As described before, $\eta$-phase, $\gamma$-phase and $\kappa$-phase, are metastable thermodynamically. Also, both $\eta$-phase and $\gamma$-phase have structural defect in their crystal structures, resulting in that these polytypes crystallize at a lower temperature, compared with $\alpha$-Al$_2$O$_3$. Since the Cr$_2$O$_3$ buffer layer has the same corundum structure as that of $\alpha$-Al$_2$O$_3$, a large amount of $\alpha$-Al$_2$O$_3$ thin film was formed on Cr$_2$O$_3$/YSZ/Si at 1323 K through hetero epitaxial growth. Figure 5 shows the effect of TMA flow rate on (a) the film deposition rate, (b) the volume fraction of each Al$_2$O$_3$ polytype and the total amount of crystalline Al$_2$O$_3$ in the unit volume, and (c) the expanded vertical axis of (b) at the lower range.

Substrate: Cr$_2$O$_3$/YSZ/Si; Deposition temperature: 1323 K; Other Deposition conditions: shown in Table 1.

![Image](image-url)

**Fig. 5.** Effects of the TMA flow rate on (a) the film deposition rate, (b) the volume fraction of each Al$_2$O$_3$ polytype and the total amount of crystalline Al$_2$O$_3$ in the unit volume, and (c) the expanded vertical axis of (b) at the lower range.

- **Table 2.** Calculated volume per one Al atom in unit cells of Al$_2$O$_3$ polytypes, $\alpha$-, $\kappa$-, and $\gamma$-Al$_2$O$_3$ at 1323 K

| Polytype    | Unit cell volume/Å$^3$ | Al atoms in the unit cell | Volume per one Al atom/Å$^3$ |
|-------------|------------------------|---------------------------|-----------------------------|
| $\alpha$-Al$_2$O$_3$ | 0.262                  | 12                        | 0.0218                      |
| $\kappa$-Al$_2$O$_3$ | 0.368                  | 16                        | 0.0230                      |
| $\gamma$-Al$_2$O$_3$ | 0.515                  | 22                        | 0.0234                      |

When increasing the TMA flow rate, the series of Al$_2$O$_3$ polytypes, $\alpha$-, $\kappa$- and $\gamma$-Al$_2$O$_3$, appeared in Fig. 5, and finally amorphous phase might be main phase with the order of decreasing the volume per one Al atom in each unit cell. This tendency arises because the higher TMA flow rate made it difficult to form the thermodynamically stable phase, i.e. a dense crystal structure: $\alpha$-Al$_2$O$_3$, under high supply rate of the raw material. On the other hand, with increase of deposition temperature, amorphous and the series of Al$_2$O$_3$ polytypes, $\eta$-, $\gamma$-, $\kappa$- and $\alpha$-Al$_2$O$_3$, appeared in Fig. 4 with the order of decreasing the volume per one Al atom in each unit cell. In this hypothesis, we should estimate the volume per one Al atom at 1323 K, 01-070-5679), $\kappa$ (ICDD 00-052-0803), and $\gamma$ (ICDD 00-056-0457) at room temperature (298 K), and the thermal expansion coefficients (TEC) data given in the literature. Since the TEC data of $\kappa$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ was limited at lower temperature range below 1323 K, the unit-cell volumes were calculated based on the extrapolated TEC data.

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Al₂O₃ polytypes and valency also must a ratios of aluminum and oxygen are supplied. This multi-

however, there is no TEC data for \(\mathrm{p-Al_2O_3}\). Therefore, the reason why the small amounts of metastable phases and a large amount of amorphous \(\mathrm{Al_2O_3}\) formed below 1323 K should be discussed from the standpoint of CVD kinetics. There are two possible reasons why metastable phases and amorphous \(\mathrm{Al_2O_3}\) formed instead of the thermodynamically stable \(\alpha\)-\(\mathrm{Al_2O_3}\). The one reason is that metastable \(\mathrm{Al_2O_3}\) polytypes or/and amorphous \(\mathrm{Al_2O_3}\) can kinetically nucleate before the nucleation of the stable \(\alpha\)-\(\mathrm{Al_2O_3}\) in thermal CVD process at lower and intermediate temperatures. The other is that the growth rate of metastable polytypes or amorphous \(\mathrm{Al_2O_3}\) is larger than that of stable \(\alpha\)-\(\mathrm{Al_2O_3}\) in CVD process at low and intermediate temperatures. On the other hand, polycrystalline \(\mathrm{Cr_2O_3}\) thin films are known to be formed on gold-coated glass at a low temperature of 673 K using CVD.\(^{22}\) Actually, \(\mathrm{Cr_2O_3}\) has no polytype such as \(\alpha\)-, \(\kappa\)-, or \(\gamma\)-type in \(\mathrm{Al_2O_3}\). The result of this, chromium has multiple valences (0 to \(+6\)).\(^{23}\) Therefore, corundum-type \(\mathrm{Cr_2O_3}\) can be deposited at lower temperatures. However, aluminum shows single ionic valence (+3). Formation of \(\mathrm{Al_2O_3}\) crystal is rather difficult. It must be arranged with stoichiometry: two aluminums and three oxygens. Amorphous \(\mathrm{Al_2O_3}\) forms easily when appropriate ratios of aluminum and oxygen are supplied. This multi-valency also must affect difficulty in \(\alpha\)-\(\mathrm{Al_2O_3}\) formation at lower temperatures.

Figure 6 shows the asymmetric (229) reciprocal-space-mapping (RSM) of \(\alpha\)-\(\mathrm{Al_2O_3}\) thin film grown on \(\mathrm{Cr_2O_3}\)/YSZ/Si substrate. From Fig. 6 and pole figure analysis (data not shown), one finds that \(\mathrm{Cr_2O_3}\) and \(\alpha\)-\(\mathrm{Al_2O_3}\) have good lattice matching, YSZ, \(\mathrm{Cr_2O_3}\) and \(\alpha\)-\(\mathrm{Al_2O_3}\) thin films were found to have epitaxial growth. Compared between the distance between the \(\alpha\)-\(\mathrm{Al_2O_3}\) (229)-planes and the distance between the \(\mathrm{Cr_2O_3}\) (229)-planes, it is seen that the film was grown with its own in-plane lattice constant. From \(2\theta-\omega\) scanning and RSM measurement, the lattice constants of \(\alpha\)-\(\mathrm{Al_2O_3}\) thin film are \(a = 4.78\,\text{Å}\) and \(c = 12.97\,\text{Å}\) at room temperature. The difference between the measured values and reference values in ICDD card No. 01-070-5679 \((a = 4.760\,\text{Å}\) and \(c = 12.993\,\text{Å}\)) gives the lattice strain such as \(\varepsilon_a = 0.42\%\) and \(\varepsilon_c = -1.7\%\) at room temperature. Possible reason for these deviations is caused by thermal stress induced by difference between \(\mathrm{Cr_2O_3}\)/YSZ/Si substrate and \(\alpha\)-\(\mathrm{Al_2O_3}\) thin film during cooling. The tensile stress by Si substrate generates in-plane \((\alpha\)-axis\) stretch and out-of-plane \((\gamma\)-axis\) shrink of \(\alpha\)-\(\mathrm{Al_2O_3}\) thin film.

The effect of different buffer layer on growth of \(\alpha\)-\(\mathrm{Al_2O_3}\) is of much interest in this study. Figure 7 shows XRD patterns of (a) epitaxial YSZ thin film deposited on (001)Si using PLD method, and (b) \(\mathrm{Al_2O_3}\) thin film on (a), (c) \(\mathrm{P-Cr_2O_3}\)/P-CeO₂/Si, (d) \(\mathrm{P-Cr_2O_3}\)/P-YSZ/Si, and (e) \(\mathrm{Cr_2O_3}\) sintered body. TMA flow rate is fixed to be \(3.3 \times 10^{-9}\,\text{m}^3\,\text{s}^{-1}\), and other deposition condition is shown in Table 1. Comparing Figs. 7(a) and 7(b), \(\kappa\)-\(\mathrm{Al_2O_3}\) thin films are grown epitaxially along the \(\gamma\)-axis on epitaxial-YSZ/001Si substrate. In case of polycrystalline \(\mathrm{Cr_2O_3}\) buffer on different substrates [Figs. 7(c) and 7(d)] or \(\mathrm{Cr_2O_3}\) sintered body as the substrates [Fig. 7(e)], there exist the polycrystalline \(\alpha\)-\(\mathrm{Al_2O_3}\) and \(\mathrm{Cr_2O_3}\) peaks with the same Miller index \((h\,k\,l)\). It is concluded that polycrystalline \(\alpha\)-\(\mathrm{Al_2O_3}\) thin film can be deposited on various substrates when it has a top buffer layer of polycrystalline \(\mathrm{Cr_2O_3}\), resulting in that each \(\mathrm{Al_2O_3}\) grains grow on \(\mathrm{Cr_2O_3}\) grains with epitaxial relation.

Figure 8 shows the estimated unit cell configuration and lattice mismatch \((f)\) between \(\mathrm{Al_2O_3}\) thin films and top buffer layer at 1323 K, at which the largest amount of \(\alpha\)-
Al$_2$O$_3$ was obtained in this study. The lattice constants of the $\alpha$-Al$_2$O$_3$, $\kappa$-Al$_2$O$_3$, Cr$_2$O$_3$, and YSZ at 1323 K were calculated using the lattice constants at room temperature by ICDD cards and the thermal expansion coefficients given in the literature. For simplicity, we ignored the effects of thermal stress by the TEC difference between the Al$_2$O$_3$ film and the substrate in this calculation. Thermodynamically, $\alpha$-Al$_2$O$_3$ is the most stable phase among the Al$_2$O$_3$ polytypes. Cr$_2$O$_3$ has the same corundum structure as that of $\alpha$-Al$_2$O$_3$. $\kappa$-Al$_2$O$_3$ has an orthorhombic lattice; YSZ has a cubic lattice. Actual calculation brings the lattice mismatch is $-4\%$ between $\alpha$-Al$_2$O$_3$ and Cr$_2$O$_3$ (as shown in Fig. 8), which is rather large for normal epitaxial growth of thin films, however, the same crystal structure (corundum) permits epitaxial growth if lattice mismatch is large.

Conversely, two $\kappa$-Al$_2$O$_3$ unit cells are possibly deposited on one Cr$_2$O$_3$ unit cell with a lower lattice mismatch, $-2.6$ and $-3.2\%$ as shown in Fig. 8. In this case, however, the difference in crystal structure might explain that the $\kappa$-Al$_2$O$_3$ film was deposited on Cr$_2$O$_3$ at limited temperatures only (Fig. 2 at 1223 K). Furthermore, this result explains the reason that the (242)$\kappa$-Al$_2$O$_3$ diffraction peak deposited on polycrystalline Cr$_2$O$_3$ buffer layer at a higher deposition temperature (1323 K) also as shown in Figs. 7(c) and 7(d).

When using YSZ as the substrate instead of Cr$_2$O$_3$, the lattice mismatch between $\alpha$-Al$_2$O$_3$ and YSZ is quite large ($-20$ and $-7.6\%$). Moreover, their crystal systems (hexagonal and orthorhombic) differ. It is difficult to configure the $\alpha$-Al$_2$O$_3$ unit cell on the YSZ unit cell with an epitaxial nature. Perhaps for this reason, $\alpha$-Al$_2$O$_3$ cannot be deposited on YSZ [Fig. 7(b)]. On the other hand, the lattice mismatch between $\kappa$-Al$_2$O$_3$ and YSZ is $-6.2$ and $7.5\%$ with suitable unit cell configurations for epitaxial film growth (two $\kappa$-Al$_2$O$_3$ unit cells deposited on three YSZ unit cells).

From these discussions, it is concluded that epitaxial growth can be estimated from both similarity in crystal structure and moderate lattice mismatch between $\alpha$-Al$_2$O$_3$ thin film and Cr$_2$O$_3$ buffered Si substrate, and between $\kappa$-Al$_2$O$_3$ and YSZ buffered Si substrate.

4. Conclusion

Using cold wall thermal CVD with TMA as a raw material, Al$_2$O$_3$ thin films were deposited on the Cr$_2$O$_3$/YSZ-buffered Si substrate. We investigated the effects of sub-

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![Fig. 7. XRD patterns of (a) YSZ/Si, and (b) Al$_2$O$_3$ thin films prepared on (a), (c) P-Cr$_2$O$_3$/CeO$_2$/Si, (d) P-Cr$_2$O$_3$/YSZ/Si, and (e) Cr$_2$O$_3$ sintered body at deposition temperature of 1323 K.](image)

![Fig. 8. Estimated unit cell alignment and lattice mismatch between Al$_2$O$_3$ thin film and top layer of buffer layers at 1323 K. Calculated based on lattice parameters from Cr$_2$O$_3$(ICDD 00-038-1479) and YSZ(ICDD 00-030-1468), and thermal expansion coefficient data.](image)
strate temperatures, deposition rates, and different buffer layers on crystallized \( \text{Al}_2\text{O}_3 \) film growth. By changing the deposition conditions, especially the deposition temperature and buffer layers, various \( \text{Al}_2\text{O}_3 \) polytypes (\( \alpha, \kappa, \gamma, \) and \( \eta \)) films and amorphous \( \text{Al}_2\text{O}_3 \) film were obtained. The \( \alpha\text{-Al}_2\text{O}_3 \) thin films were grown epitaxially on \( \text{Cr}_2\text{O}_3/\text{YSZ} \) buffered Si substrate at 1323 K. The \( \text{Cr}_2\text{O}_3 \) buffer layer brought epitaxial \( \alpha\text{-Al}_2\text{O}_3 \) film growth. When the \( \text{P} \)(polycrystalline)-\( \text{Cr}_2\text{O}_3 \) top buffer layer was used, P-\( \alpha\text{-Al}_2\text{O}_3 \) films were made on P-\( \text{Cr}_2\text{O}_3/\text{CeO}_2/\text{Si} \), P-\( \text{Cr}_2\text{O}_3/\text{P}-\text{YSZ}/\text{Si} \), and \( \text{Cr}_2\text{O}_3 \) sintered bodies. The crystal orientations of the three P-\( \alpha\text{-Al}_2\text{O}_3 \) films were slightly different, but the crystal orientation was strongly inherited by that of the continuing P-\( \text{Cr}_2\text{O}_3 \). The \( \text{Cr}_2\text{O}_3 \) buffer layer played very important roles for growing \( \alpha\text{-Al}_2\text{O}_3 \). In conclusion, epitaxial growth can be explained by both similarity in crystal structure and moderate lattice mismatch between \( \text{Al}_2\text{O}_3 \) thin film and \( \text{Cr}_2\text{O}_3 \) buffered Si substrate.

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