FULL PAPER

Effect of deposition conditions and buffer layers on amorphous or polytype phase formation in Al_2O_3 thin films by chemical vapor deposition using tri-methyl aluminum

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Al_2O_3 thin films were deposited on (001)Si substrate through Cr_2O_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_2O_3 thin films were formed. At lower temperatures (1123–1173 K), η - Al_2O_3 and amorphous Al_2O_3 were found in mixture. With increasing the deposition temperature, the series of Al_2O_3 polytypes (γ , κ and α) appeared in the order of decreasing the unit cell volume per Al atom. At 1323 K, single-phase α - Al_2O_3 thin film was obtained in success. On (001) Cr_2O_3 /YSZ/Si substrate, epitaxial (001) α - Al_2O_3 thin-film was grown, however, on (001)YSZ/Si substrate, epitaxial (001) κ - Al_2O_3 thin film was formed. It shows that buffer layer also has much influence on polytype of Al_2O_3 thin film. On the other hand, there exist the polycrystalline α - Al_2O_3 and Cr_2O_3 have the same Miller index ($h\ k\ l$), therefore, polycrystalline α - Al_2O_3 thin film was deposited on the polycrystalline Cr_2O_3 buffer layer in which each Al_2O_3 and Cr_2O_3 grain has an epitaxial relation. This epitaxial growth can be explained by both the similarity in crystal structure between Al_2O_3 film and Cr_2O_3 buffer layer, and also their moderate lattice mismatch.

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1. Introduction

Among the various polytypes of Al_2O_3 such as α , κ , γ , θ , η , δ , and χ phases,¹⁾ α phase is only stable and the others are metastable with higher Gibbs formation energies.²⁾ Higher temperatures than around 1473 K are necessary to form α - Al_2O_3 after formation of other polytypes or amorphous phase.³⁾ As cutting tool coating materials, metastable κ - Al_2O_3 and stable α - Al_2O_3 are used because of their high hardness and heat resistance.^{4),5)} To make these Al_2O_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,⁶⁾ aluminum chloride (AlCl_3),^{4),5),7),8)} aluminum acetylacetonate [$\text{Al}(\text{acac})_3$],⁹⁾ and tri-methyl aluminum [TMA,

$\text{Al}(\text{CH}_3)_3$].^{10)–14)} AlCl_3 have been used for α - Al_2O_3 thin film with CO_2 - H_2 by thermal CVD in cutting tools industry since the 1970 s.⁷⁾ 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.^{4),5),7)} However, the obtained Al_2O_3 thin films deposited at lower temperatures tend to include chlorine residue.⁸⁾

Recently, much attention has been paid to TMA [$\text{Al}(\text{CH}_3)_3$] as aluminum source. By atomic layer deposition,^{11)–13)} dense and amorphous Al_2O_3 thin-films can be obtained. By plasma-enhanced CVD,¹⁰⁾ γ - Al_2O_3 thin films were deposited with N_2O as an oxidizing agent on Si substrate. By thermal CVD,¹⁴⁾ γ - Al_2O_3 thin films were also deposited with O_2 on GaN. However, no report describes α - Al_2O_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_2O_3 thin films (corundum structure) were grown epitaxially on yttria-stabilized-zirconia (YSZ) buffered (001)Si substrate using pulsed laser deposition (PLD) method.¹⁵⁾ Similarly, by sputtering method,¹⁶⁾ polycrystalline α - Al_2O_3 thin film was deposited on polycrystalline Cr_2O_3 -buffered Si substrate in which each Al_2O_3

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and Cr_2O_3 grains have an epitaxial relation. No report, however, has described $\alpha\text{-Al}_2\text{O}_3$ thin film deposited on $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$ substrate using CVD so far. If $\alpha\text{-Al}_2\text{O}_3$ thin film is deposited on a Cr_2O_3 -buffered Si substrate by CVD method, it must be useful information for next-generation cutting tool coating.

In this study, Al_2O_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_2O_3 polytype 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, $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$, P- $\text{Cr}_2\text{O}_3/\text{P-CeO}_2/\text{Si}$, and P- $\text{Cr}_2\text{O}_3/\text{P-YSZ}/\text{Si}$, 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 ($298 \pm 5 \text{ K}$) using PLD, then annealed at 1373 K for $1.8 \times 10^4 \text{ s}$. The other buffer layers were also deposited by PLD using a KrF excimer laser ($\lambda = 248 \text{ nm}$) at the substrate temperature of 1023 K in vacuum with oxygen partial pressure of $7.33 \times 10^{-2} \text{ Pa}$. The laser fluence and the repetition rate were approximately 1.2 J cm^{-2} and 7 Hz, respectively. The YSZ, Cr_2O_3 , and CeO_2 targets for PLD were fabricated by solid-state sintering. That is, YSZ (8 at% Y_2O_3 –92 at% ZrO_2), Cr_2O_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 $1.08 \times 10^4 \text{ s}$, at 1573 K for $2.16 \times 10^4 \text{ s}$, and at 1573 K for $5.4 \times 10^4 \text{ s}$. In addition to the buffered Si substrates above, a Cr_2O_3 sintered body was used as the substrate.

On these substrates, Al_2O_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 ($50 \text{ mm} \phi \times 31 \text{ mm}$, 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 calibra-

tion, actual substrate temperatures were measured using a K-type thermocouple attached on the upper surface of Si substrate with $10 \times 10 \times 0.5 \text{ mm}^3$ with Al_2O_3 -based cement paste (Aron Ceramics; Toagosei Chemical Industry Co. Ltd., Japan).

The film thickness was measured with a surface profilometer (Dektek³); Sloan Technology Corp., USA). The phases and crystallinity of the deposited films were evaluated using X-ray diffractometer (XRD, MPD; Malvern PANalytical, Netherland) with $\text{Cu K}\alpha$ 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_2O_3 polytype is shown in **Figure 2**. This is the case of $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$ substrate (both Cr_2O_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_2O_3 and (001)YSZ. The former epitaxial growth is well-known to us.¹⁷⁾ The latter epitaxial growth has a twin domain in the c -axis direction.¹⁵⁾ Figures 2(b)–2(f) show the change in Al_2O_3 polytype depending on the deposition temperatures. At 1123 and 1173 K, $\eta\text{-Al}_2\text{O}_3$ are detected. The mixed phases of κ - and $\gamma\text{-Al}_2\text{O}_3$ are detected at 1223 K. κ , γ , and $\alpha\text{-Al}_2\text{O}_3$ are detected at 1273 K. Only $\alpha\text{-Al}_2\text{O}_3$ is observed at 1323 K. It reveals that single-phase $\alpha\text{-Al}_2\text{O}_3$ thin-film can be obtained by thermal CVD with TMA.

Figure 3 shows the relation between the deposition rate of Al_2O_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-

Table 1. Deposition conditions for Al_2O_3 thin film by cold-wall type thermal CVD process

Deposition temperature	1123–1323 K
Chamber pressure	133.32 Pa
TMA vaporizer temperature	303 K
Flow rate of TMA	3.3×10^{-9} – $5.0 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$
Flow rate of O_2 gas	$1.26 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Flow rate of Ar gas	$1.26 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Deposition time	$3.6 \times 10^2 \text{ s}$

Fig. 1. Schematic diagram of cold-wall type thermal CVD.

Fig. 2. XRD patterns of (a) $\text{Cr}_2\text{O}_3/\text{YSZ}$ -buffered Si substrate and (b)–(f) Al_2O_3 thin films prepared on $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$ with 1123–1323 K deposition temperature. Substrate: $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$, TMA flow rate: $3.3 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$, Other deposition conditions: shown in Table 1.

Fig. 3. Effects of deposition temperature on deposition rate of Al_2O_3 thin film deposited on $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$ substrate by CVD.
Substrate: $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$, TMA flow rate: $3.3 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$, Other deposition conditions: shown in Table 1.

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 Al_2O_3 deposition rate as a function of the deposition temperature has a maximum as shown in Fig. 3.

It is well known that amorphous Al_2O_3 decreased the strength of Al_2O_3 -coated cutting tools.¹⁸⁾ Therefore, the Al_2O_3 film is needed in industry containing higher amounts

Fig. 4. Effects of deposition temperature of Al₂O₃ thin film on (a) volume fraction of each Al₂O₃ polytype in the unit volume of thin film and the total amount of crystalline Al₂O₃ in thin film and (b) lower volume range of Al₂O₃ polytypes in thin film.

Substrate: Cr₂O₃/YSZ/Si, TMA flow rate: $3.3 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$, Other deposition conditions: shown in Table 1.

of crystalline Al₂O₃ polytypes, especially α or κ -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 α -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.

[Summation of each Al₂O₃-polytype volume fraction in unit volume of thin film]

$$\propto \frac{1}{t} \left(\frac{I_{\alpha(0012)}}{|F_{\alpha(0012)}|^2} + \frac{I_{\kappa(006)}}{|F_{\kappa(006)}|^2} + \frac{I_{\gamma(333)}}{|F_{\gamma(333)}|^2} + \frac{I_{\eta(333)}}{|F_{\eta(333)}|^2} \right)$$

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 α -Al₂O₃ fraction. Figure 4(b) shows an enlargement of Fig. 4(a) at the lower volume fraction. At 1123 to 1173 K, the η -Al₂O₃ polytype is the dominant crystallized phase of the film. The κ -Al₂O₃ and γ -Al₂O₃ are formed at 1223 K. However, α -Al₂O₃ is the main fraction together with a small amount of κ -Al₂O₃ and γ -Al₂O₃ at 1273 K. Finally, a large amount of α -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 η -phase and the large amount of amorphous phase were deposited at lower deposition temperatures (1123 and 1173 K). Similarly, small amounts of κ -phase and large amounts of amorphous phase were deposited at intermediate deposition temperature (1223 K). At higher deposition temperatures (1273 and 1323 K), larger

Fig. 5. Effects of the TMA flow rate on (a) the film deposition rate, (b) the volume fraction of each Al_2O_3 polytype and the total amount of crystalline Al_2O_3 in the unit volume, and (c) the expanded vertical axis of (b) at the lower range.

Substrate: $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$, Deposition temperature: 1323 K, Other Deposition conditions: shown in Table 1.

amounts of α - Al_2O_3 were deposited on the $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$ substrate. These results agree well to Fig. 2. As described before, η -phase, γ -phase and κ -phase, are metastable thermodynamically. Also, both η -phase and γ -phase have structural defect in their crystal structures, resulting in that these polytypes crystallize at a lower temperature, compared with α - Al_2O_3 . Since the Cr_2O_3 buffer layer has the same corundum structure as that of α - Al_2O_3 ,¹⁶⁾ a large amount of α - Al_2O_3 thin film was formed on $\text{Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$ at 1323 K through hetero epitaxial growth.

Figure 5 shows the effect of TMA flow rate on (a) the film deposition rate, and (b) volume fractions of each Al_2O_3 polytype and (c) the total amount of crystalline Al_2O_3 polytypes in the unit volume, which are calculated in the same way in Fig. 4. From this figure (a), the deposition rate is approximately constant at a TMA flow rate below $4.3 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$, and then the deposition rate rapidly increases at a range of 4.7×10^{-9} to $5.0 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$. At the same time, the summation of each Al_2O_3 polytype decreases. In this deposition condition, the α - Al_2O_3 is dominant in the crystalline phase, so the amount of α - Al_2O_3 decreases with the increasing TMA flow rate, although κ - Al_2O_3 formed above $3.8 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$ and γ - Al_2O_3 formed above $4.3 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$. Table 2 shows the volume per one Al atom in a unit cell at 1323 K. The unit cell volumes of the α - Al_2O_3 , κ - Al_2O_3 , and γ - Al_2O_3 at 1323 K were calculated using the International Centre for Diffraction Data (ICDD) crystal structure data α (ICDD

Table 2. Calculated volume per one Al atom in unit cells of Al_2O_3 polytypes, α -, κ -, and γ - Al_2O_3 at 1323 K

	α - Al_2O_3	κ - Al_2O_3	γ - Al_2O_3
Unit cell volume/nm ³	0.262	0.368	0.515
Al atoms in the unit cell	12	16	22
Volume per one Al atom/nm ³	0.0218	0.0230	0.0234

01-070-5679), κ (ICDD 00-052-0803), and γ (ICDD 00-056-0457) at room temperature (298 K), and the thermal expansion coefficients (TEC) data given in the literature.^{19)–21)} Since the TEC data of κ - Al_2O_3 and γ - Al_2O_3 was limited at lower temperature range below 1323 K, the unit-cell volumes were calculated based on the extrapolated TEC data.

When increasing the TMA flow rate, the series of Al_2O_3 polytypes, α -, κ - and γ - Al_2O_3 , appeared in Fig. 5, and finally amorphous phase might be main phase with the order of increasing 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: α - Al_2O_3 , under high supply rate of the raw material. On the other hand, with increase of deposition temperature, amorphous and the series of Al_2O_3 polytypes, η -, γ -, κ - and α - Al_2O_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,

Fig. 6. Reciprocal space mapping of α - Al_2O_3 / Cr_2O_3 /YSZ/Si thin film. Substrate: Cr_2O_3 /YSZ/Si, Deposition temperature: 1323 K, Other Deposition condition: Table 1.

however, there is no TEC data for η - Al_2O_3 . Therefore, the reason why the small amounts of metastable phases and a large amount of amorphous 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 Al_2O_3 formed instead of the thermodynamically stable α - Al_2O_3 . The one reason is that metastable Al_2O_3 polytypes and/or amorphous Al_2O_3 can kinetically nucleate before the nucleation of the stable α - Al_2O_3 in thermal CVD process at lower and intermediate temperatures. The other is that the growth rate of metastable polytypes or amorphous Al_2O_3 is larger than that of stable α - Al_2O_3 in CVD process at low and intermediate temperatures. On the other hand, polycrystalline 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, Cr_2O_3 has no polytype such as α -, κ -, or γ -type in Al_2O_3 . The result of this, chromium has multiple valences (0 to +6).²³⁾ Therefore, corundum-type Cr_2O_3 can be deposited at lower temperatures. However, aluminum shows single ionic valence (+3). Formation of Al_2O_3 crystal is rather difficult. It must be arranged with stoichiometry: two aluminums and three oxygens. Amorphous Al_2O_3 forms easily when appropriate ratios of aluminum and oxygen are supplied. This multi-valency also must affect difficulty in α - Al_2O_3 formation at lower temperatures.

Figure 6 shows the asymmetric (229) reciprocal-space-mapping (RSM) of α - Al_2O_3 thin film grown on Cr_2O_3 /YSZ/Si substrate. From Fig. 6 and pole figure analysis (data not shown), one finds that Cr_2O_3 and α - Al_2O_3 have good lattice matching, YSZ, Cr_2O_3 and α - Al_2O_3 thin films were found to have epitaxial growth. Compared between the distance between the α - Al_2O_3 (229)-planes and the distance between the Cr_2O_3 (229)-planes, it is seen that the

film was grown with its own in-plane lattice constant. From 2θ - ω scanning and RSM measurement, the lattice constants of α - Al_2O_3 thin film are $a = 4.78 \text{ \AA}$ and $c = 12.97 \text{ \AA}$ at room temperature. The difference between the measured values and reference values in ICDD card No. 01-070-5679 ($a = 4.760 \text{ \AA}$ and $c = 12.993 \text{ \AA}$) 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 Cr_2O_3 /YSZ/Si substrate and α - Al_2O_3 thin film during cooling. The tensile stress by Si substrate generates in-plane (a -axis) stretch and out-of-plane (c -axis) shrink of α - Al_2O_3 thin film.

The effect of different buffer layer on growth of α - 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) Al_2O_3 thin film on (a), (c) P- Cr_2O_3 /P-CeO₂/Si, (d) P- Cr_2O_3 /P-YSZ/Si, and (e) 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), κ - Al_2O_3 thin films are grown epitaxially along the c -axis on epitaxial-YSZ/(001)Si substrate. In case of polycrystalline Cr_2O_3 buffer on different substrates [Figs. 7(c) and 7(d)] or Cr_2O_3 sintered body as the substrates [Fig. 7(e)], there exist the polycrystalline α - Al_2O_3 and Cr_2O_3 peaks with the same Miller index ($h k l$). It is concluded that polycrystalline α - Al_2O_3 thin film can be deposited on various substrates when it has a top buffer layer of polycrystalline Cr_2O_3 , resulting in that each Al_2O_3 grains grow on Cr_2O_3 grains with epitaxial relation.

Figure 8 shows the estimated unit cell configuration and lattice mismatch (f) between Al_2O_3 thin films and top buffer layer at 1323 K, at which the largest amount of α -

Al_2O_3 was obtained in this study. The lattice constants of the $\alpha\text{-Al}_2\text{O}_3$, $\kappa\text{-Al}_2\text{O}_3$, Cr_2O_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.^{19),20),24)} For simplicity, we ignored the effects of thermal stress by the TEC difference between the Al_2O_3 film and the substrate in this calculation. Thermodynamically, $\alpha\text{-Al}_2\text{O}_3$ is the most stable phase among the Al_2O_3 polytypes. Cr_2O_3 has the same corundum structure as that of $\alpha\text{-Al}_2\text{O}_3$. $\kappa\text{-Al}_2\text{O}_3$ has an orthorhombic lattice; YSZ has a cubic lattice. Actual calculation brings

the lattice mismatch is -4% between $\alpha\text{-Al}_2\text{O}_3$ and Cr_2O_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 $\kappa\text{-Al}_2\text{O}_3$ unit cells are possibly deposited on one Cr_2O_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 $\kappa\text{-Al}_2\text{O}_3$ film was deposited on Cr_2O_3 at limited temperatures only (Fig. 2 at 1223 K). Furthermore, this result explains the reason that the $(242)\kappa\text{-Al}_2\text{O}_3$ diffraction peak deposited on polycrystalline Cr_2O_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_2O_3 , the lattice mismatch between $\alpha\text{-Al}_2\text{O}_3$ and YSZ is quite large (-20 and -7.6%). Moreover, their crystal systems (hexagonal and orthorhombic) differ. It is difficult to configure the $\alpha\text{-Al}_2\text{O}_3$ unit cell on the YSZ unit cell with an epitaxial nature. Perhaps for this reason, $\alpha\text{-Al}_2\text{O}_3$ cannot be deposited on YSZ [Fig. 7(b)]. On the other hand, the lattice mismatch between $\kappa\text{-Al}_2\text{O}_3$ and YSZ is -6.2 and 7.5% with suitable unit cell configurations for epitaxial film growth (two $\kappa\text{-Al}_2\text{O}_3$ 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 $\alpha\text{-Al}_2\text{O}_3$ thin film and Cr_2O_3 buffered Si substrate, and between $\kappa\text{-Al}_2\text{O}_3$ and YSZ buffered Si substrate.

4. Conclusion

Using cold wall thermal CVD with TMA as a raw material, Al_2O_3 thin films were deposited on the $\text{Cr}_2\text{O}_3/\text{YSZ}$ -buffered Si substrate. We investigated the effects of sub-

Fig. 7. XRD patterns of (a) YSZ/Si, and (b) Al_2O_3 thin films prepared on (a), (c) $\text{P-Cr}_2\text{O}_3/\text{CeO}_2/\text{Si}$, (d) $\text{P-Cr}_2\text{O}_3/\text{YSZ}/\text{Si}$, and (e) Cr_2O_3 sintered body at deposition temperature of 1323 K.

Fig. 8. Estimated unit cell alignment and lattice mismatch between Al_2O_3 thin film and top layer of buffer layers at 1323 K.

Calculated based on lattice parameters from Cr_2O_3 (ICDD 00-038-1479) and YSZ (ICDD 00-030-1468), and thermal expansion coefficient data.

strate temperatures, deposition rates, and different buffer layers on crystallized Al₂O₃ film growth. By changing the deposition conditions, especially the deposition temperature and buffer layers, various Al₂O₃ polytypes (α , κ , γ , and η) films and amorphous Al₂O₃ film were obtained. The α -Al₂O₃ thin films were grown epitaxially on Cr₂O₃/YSZ buffered Si substrate at 1323 K. The Cr₂O₃ buffer layer brought epitaxial α -Al₂O₃ film growth. When the P(polycrystalline)-Cr₂O₃ top buffer layer was used, P- α -Al₂O₃ films was made on P-Cr₂O₃/CeO₂/Si, P-Cr₂O₃/P-YSZ/Si, and Cr₂O₃ sintered bodies. The crystal orientations of the three P- α -Al₂O₃ films were slightly different, but the crystal orientation was strongly inherited by that of the continuing P-Cr₂O₃. The Cr₂O₃ buffer layer played very important roles for growing α -Al₂O₃. In conclusion, epitaxial growth can be explained by both similarity in crystal structure and moderate lattice mismatch between Al₂O₃ thin film and Cr₂O₃ buffered Si substrate.

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