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Preparation of $\text{HfO}_2\text{-Al}_2\text{O}_3$ nanocomposite films using chemical vapor deposition

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We prepared $\text{HfO}_2\text{-Al}_2\text{O}_3$ nanocomposite films using chemical vapor deposition. Fibrous and lamellar microstructures formed in the monoclinic and tetragonal HfO_2 ($m/t\text{-HfO}_2$)- $\alpha\text{-Al}_2\text{O}_3$ films at deposition temperature of 1573 K and Al mole fraction in the precursor vapor of 36–74 mol % Al_2O_3 . Characterization by electron microscopy revealed that the $m/t\text{-HfO}_2$ fibrous and lamellar structures are present throughout the $\alpha\text{-Al}_2\text{O}_3$ columnar matrix above 50 mol % Al_2O_3 (55 vol % Al_2O_3), while $\alpha\text{-Al}_2\text{O}_3$ lamellar structure was formed in $m\text{-HfO}_2$ matrix below 50 mol % Al_2O_3 .

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1. Introduction

Zirconia (ZrO_2) is widely used in structural ceramics and thermal barrier coatings due to its low thermal conductivity ($1.5\text{--}3.0\text{ W m}^{-1}\text{ K}^{-1}$) and high fracture toughness ($2\text{--}14\text{ MPa m}^{0.5}$).^{1,2)} The mechanical properties of ZrO_2 can be enhanced by synthesizing composites with alumina ($\alpha\text{-Al}_2\text{O}_3$), namely zirconia-toughened alumina^{3)–6)} or the $\text{ZrO}_2\text{-Al}_2\text{O}_3$ eutectic.^{7)–11)} These composites have been widely studied in the form of bulk samples prepared using sintering and melt-solidification techniques.

Hafnia (HfO_2) has similar properties and crystallographic features as ZrO_2 . Because HfO_2 has a higher melting point (3100 K) and higher monoclinic–tetragonal transition point (2200 K) than ZrO_2 ,¹²⁾ HfO_2 -based ceramics are candidate materials for environmental barrier coatings.^{13,14)} In addition to HfO_2 -based ceramics, $\text{HfO}_2\text{-Al}_2\text{O}_3$ eutectic composites have also been prepared using melt-solidification methods such as floating zone method¹⁵⁾ and micro-pulling-down technique.¹⁶⁾

To make use of the excellent mechanical and thermal properties of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ and $\text{HfO}_2\text{-Al}_2\text{O}_3$ composites in the form of coatings, a feasible deposition technique must be established. We have previously reported on chemical vapor deposition (CVD) of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ nanocomposite films, which exhibited high hardness and high thermal insulating properties.¹⁷⁾ In addition, HfO_2 films exhibited self-

oriented growth, and transparent HfO_2 thick films can be obtained by a high-speed epitaxial growth technique.^{18),19)}

In the present study, we demonstrated CVD of $\text{HfO}_2\text{-Al}_2\text{O}_3$ nanocomposite films, we characterized the effects of deposition conditions on phase, and the microstructure of the films was investigated. Results for several temperature-composition combinations were plotted to create a CVD phase diagram for this system.

2. Experimental procedure

A schematic of the CVD apparatus has been described elsewhere.²⁰⁾ Metal-organic compounds of $\text{Hf}(\text{acac})_4$ (acac: acetylacetonate) (Mitsuwa Chemicals Co., Ltd.) and $\text{Al}(\text{acac})_3$ (Sigma-Aldrich Co. LLC) were maintained at temperatures of 443–473 and 433–483 K, respectively, in the precursor furnaces. Emitted precursor vapor was transferred to the deposition chamber using Ar as a carrier gas. O_2 gas was introduced separately into the chamber through a double-tube nozzle. Total chamber pressure was maintained at 200 Pa. The Al mole fraction in the precursor vapor ($C_{\text{Al}_2\text{O}_3}$) was calculated from the mass change of each precursor during the course of a run, expressed in terms of an oxide (mol % Al_2O_3) for the competitiveness with equilibrium phase diagrams. Stoichiometry was controlled by varying the vaporization temperatures of the precursor sources.

A polycrystalline AlN plate (8 mm × 8 mm × 1 mm) was used as a substrate. A continuous-wave diode laser (wavelength: $\lambda = 976\text{ nm}$; output power: 50–170 W; Lumics GmbH, LU0976C170) was used to irradiate the substrate through a fused quartz window, heating it to temperatures from 943 to 1573 K. The deposition temperature (T_{dep}) was

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measured using an optical pyrometer. Depositions were run for 0.6 ks.

The phase composition of the resultant films was determined by X-ray diffraction (XRD; Bruker D2 Phaser) using CuK α radiation, generated at 30 kV and 10 mA. Backscattered electron (BSE) imaging of cross-sectional and surface microstructures was performed using a field-emission scanning electron microscope (FE-SEM; Hitachi SU8010) operated 15 keV. An energy dispersive X-ray spectrometer integrated with the SEM (SEM-EDX; JEOL JSM-6510LA) and operated at an accelerating voltage of 20 kV was used to determine composition of the films. SEM-EDX analysis was performed at 10 separate points on the surface of each film. The cross-sectional microstructure was observed using a transmission electron microscope (TEM; FEI Titan 80-300) equipped with an image corrector and a high-angle annular dark-field (HAADF) detector and operated at 300 keV. The lamella for TEM analysis was prepared using a focused ion beam system (FEI Versa 3D Dual Beam).

The volume fraction (V_t) of the tetragonal HfO₂ phase (t -HfO₂) to the monoclinic HfO₂ (m -HfO₂) phase was estimated using the following formulas:^{21),22)}

$$x_t = \frac{I_t(101)}{I_m(11\bar{1}) + I_m(111)} \quad (1)$$

$$V_t = \frac{x_t}{1.311 - 0.311x_t} \quad (2)$$

where $I_t(hkl)$ and $I_m(hkl)$ are the integrated intensities of the hkl peaks for the t -HfO₂ and m -HfO₂ phases in the XRD patterns, respectively. The crystalline size (D_t) of the t -HfO₂ phase was estimated using the Scherrer equation:

$$D_t = \frac{K\lambda}{B \cos \theta} \quad (3)$$

where K , λ , B , θ are the Scherrer constant (0.9), the X-ray wavelength (0.154 nm), the full width at half maximum of the peak, and the Bragg angle, respectively, of the t -HfO₂ 101 peak. The apparent volume fraction of Al₂O₃ in the film ($V_{Al_2O_3}$) was calculated as the theoretical volume fraction of the α -Al₂O₃ phase to that of the m -HfO₂ by assuming m -HfO₂- α -Al₂O₃ pseudo-binary composite films for the sake of simplicity.

3. Results and discussion

3.1 Phase composition of HfO₂-Al₂O₃ films

Figure 1 shows the relationship between Al mole fraction in the vapor versus that in the film for deposition temperatures of 1323 and 1573 K. The Al mole fraction in the film increased linearly with the increase of that in the vapor, indicating that the Al mole fraction in the film can be directly controlled by varying the vaporization temperatures of each precursor, regardless of the deposition temperature.

Monolithic m -HfO₂ and α -Al₂O₃ films were obtained at both ends of the compositional space (0 and 100 mol %Al₂O₃, respectively). At deposition temperatures of 1573 and 1373 K, m -HfO₂- α -Al₂O₃ composite films

Fig. 1. Relationship between the Al mole fraction in the vapor ($C_{Al_2O_3}$) and in the CVD film ($c_{Al_2O_3}$).

Fig. 2. XRD patterns of the HfO₂-Al₂O₃ nanocomposite films prepared at various deposition temperatures and Al mole fractions in the vapor: (a) 1573 K and 60 mol %Al₂O₃, (b) 1323 K and 63 mol %Al₂O₃, and (c) 1193 K and 64 mol %Al₂O₃.

resulted. Above 49 mol %Al₂O₃, the t -HfO₂ phase was also present in the m -HfO₂- α -Al₂O₃ nanocomposite films [Fig. 2(a)]. At deposition temperatures of 1373 and 1173 K, XRD patterns were indexed with a mixture of t - and m -HfO₂ phases (m/t -HfO₂) and the m -HfO₂ phase, respectively, with no Al₂O₃ peaks, suggesting that the Al₂O₃ phase was amorphous [Figs. 2(b) and 2(c)].

Figure 3 summarizes the relationship between the Al mole fraction in the vapor and the apparent Al₂O₃ volume fraction in the film, the calculated m/t -HfO₂ volume fractions, and the t -HfO₂ crystallite size in the films. At deposition temperatures of 1373–1573 K, HfO₂ exhibited a monoclinic phase below 40 mol %Al₂O₃, whereas t -HfO₂

Fig. 3. Effect of the Al volume fraction in the vapor ($C_{Al_2O_3}$) and the deposition temperature (T_{dep}) on the m -HfO₂ volume fraction (V_m) and the t -HfO₂ grain size (V_t) in the HfO₂-Al₂O₃ nanocomposite films.

Fig. 4. (a, c) Cross-sectional and (b, d) surface BSE-SEM images of the m -HfO₂ and α -Al₂O₃ films prepared at 1573 K.

Fig. 5. (a, c, e) Cross-sectional and (b, d, f) surface BSE-SEM images of the HfO₂-Al₂O₃ nanocomposite films prepared at 1573 K and various Al mole fractions in the vapor: (a, b) 36 mol % Al₂O₃, (c, d) 60 mol % Al₂O₃, and (e, f) 74 mol % Al₂O₃. The white and gray contrast correspond to the HfO₂ and Al₂O₃ phases, respectively.

co-existed in the m -HfO₂- α -Al₂O₃ films above 50 mol % Al₂O₃. As the deposition temperature decreased from 1573 to 1323 K, the t -HfO₂ volume fraction was increased from 5 to 87 %, with a decline in the t -HfO₂ crystallite size from 36 to 12 nm.

3.2 Microstructure of HfO₂-Al₂O₃ films

Monolithic m -HfO₂ and α -Al₂O₃ films exhibited columnar structures with pyramidal and polygonal surface facets

(**Fig. 4**). HfO₂-Al₂O₃ films prepared at 1573 K and 36–74 mol % Al₂O₃ showed fuzzy columnar structures in cross-sections (**Fig. 5**). High-magnification BSE-SEM images and surface observations revealed fibrous and lamellar structures in the HfO₂-Al₂O₃ films, with the light and dark contrast corresponding to Hf and Al. A lamellar α -Al₂O₃ microstructure was formed in the m -HfO₂ columnar matrix at 36 mol % Al₂O₃ [Figs. 5(a) and 5(b)], while fibrous and lamellar m -HfO₂ microstructures grew inside the α -Al₂O₃

Fig. 6. (a) Cross-sectional HAADF-STEM image of the $m/t\text{-HfO}_2\text{-}\alpha\text{-Al}_2\text{O}_3$ nanocomposite film prepared at 1573 K and 60 mol % Al_2O_3 . (b) Highly magnified image of the rectangle region noted in (a), and (c) STEM-EDX elemental mapping of the intensity of the $\text{Al-K}\alpha$ and $\text{Hf-M}\beta$ lines. (d) SAED pattern of the circular region noted in (a), with enlarged regions of peaks of interest, marked by i–iv, along with axes indicating crystal orientation of the indexed phases. (e) Schematic illustrations of the crystal structures of the $m\text{-HfO}_2$ viewed along the $[0\bar{1}2]$ and $[012]$ zone axes, the $t\text{-HfO}_2$ $[2\bar{2}1]$, and $\alpha\text{-Al}_2\text{O}_3$ along $[1\bar{1}1]$.

columnar matrix at 60 and 74 mol % Al_2O_3 [Figs. 5(c)–5(f)]. Deposition rates of the $\text{HfO}_2\text{-Al}_2\text{O}_3$ films prepared at 1573 K were 101–299 $\mu\text{m h}^{-1}$.

TEM observation revealed that the fibrous and lamellar composite structures of HfO_2 were developed throughout the entire columnar grains of the Al_2O_3 matrix [Figs. 6(a) and 6(b)]. Scanning TEM (STEM)–EDX characterization confirmed a monodirectional texture constituted of HfO_2 and Al_2O_3 nanoscale grains [Fig. 6(c)]. No stabilizer element such as Y or Ca was identified in the EDX spectrum. The selected-area electron diffraction (SAED) pattern was indexed with zone axes of $m\text{-HfO}_2$ $[0\bar{1}2]$, $m\text{-HfO}_2$ $[012]$, $t\text{-HfO}_2$ $[2\bar{2}1]$, and $\alpha\text{-Al}_2\text{O}_3$ $[1\bar{1}1]$, suggesting that the orientation relationship among $m\text{-HfO}_2$, $t\text{-HfO}_2$, and $\alpha\text{-Al}_2\text{O}_3$ is $(100)_m\text{-HfO}_2 \parallel (110)_t\text{-HfO}_2 \parallel (110)_\alpha\text{-Al}_2\text{O}_3$, as depicted in Fig. 6(d). The orientation relationship between the $m\text{-HfO}_2$ and $t\text{-HfO}_2$ phases was close to the crystallographic

relationships between them, namely $(100)_m \parallel (110)_t$ and $(010)_m \parallel (001)_t$.²³⁾ Fig. 6(e) shows schematic illustrations of each phase projected along its corresponding zone axis. One of the close-packed planes of oxygen ions—i.e., the $m\text{-HfO}_2$ (100) , $t\text{-HfO}_2$ (110) , and $\alpha\text{-Al}_2\text{O}_3$ (110) planes—was parallel to the matrix growth direction, while the others, e.g., the $m\text{-HfO}_2$ $\{121\}$, $t\text{-HfO}_2$ $\{012\}$, and $\alpha\text{-Al}_2\text{O}_3$ $\{123\}$ planes, were perpendicular to the lamellar growth direction. The angles of lamellar growth directions from the film growth direction remained almost constant through the film thickness, as depicted in Fig. 6(a).

3.3 Phase and microstructure of $\text{HfO}_2\text{-Al}_2\text{O}_3$ films

Figure 7 summarizes the effects of the Al mole fraction in the vapor and of the deposition temperature on the phase composition and microstructure of the $\text{HfO}_2\text{-Al}_2\text{O}_3$

Fig. 7. (a) Equilibrium phase diagram of the $\text{HfO}_2\text{--Al}_2\text{O}_3$ pseudo-binary system and (b) effects of the Al mole fraction in the vapor ($C_{\text{Al}_2\text{O}_3}$) and the deposition temperature (T_{dep}) on the phase composition and microstructure of the $\text{HfO}_2\text{--Al}_2\text{O}_3$ nanocomposite films. m, t, and α denote $m\text{-HfO}_2$, $t\text{-HfO}_2$, and $\alpha\text{-Al}_2\text{O}_3$ phases, respectively.

nanocomposite films. The end-member $m\text{-HfO}_2$ and $\alpha\text{-Al}_2\text{O}_3$ films (0 and 100 mol % Al_2O_3 , respectively) exhibited a columnar structure. For films prepared below 50 mol % Al_2O_3 (55 vol % Al_2O_3) and at deposition temperatures of 1373 and 1573 K, the $t\text{-HfO}_2$ grains co-existed with the $m\text{-HfO}_2\text{--}\alpha\text{-Al}_2\text{O}_3$ films. In the film with an amorphous Al_2O_3 matrix deposited at 1373 K, the $t\text{-HfO}_2$ phase was stabilized.

In the $\text{ZrO}_2\text{--Al}_2\text{O}_3$ system, Deb et al. reported that tetragonal ZrO_2 stabilization by forming a $\text{ZrO}_2\text{--Al}_2\text{O}_3$ solid solution was unlikely to take place because the ionic radius of Al^{3+} (0.068 nm) is far smaller in comparison to that of Zr^{4+} (0.084 nm),²⁴⁾ the case is believed to be the same for the $\text{HfO}_2\text{--Al}_2\text{O}_3$ system (Hf^{4+} : 0.083 nm). On the other hand, stabilization of the tetragonal phase over the monoclinic one in nanocrystalline grains with no additives has been reported for both ZrO_2 ^{24),25)} and HfO_2 .^{27),28)} Although the critical crystalline size of HfO_2 might be smaller than that of ZrO_2 (30 nm) due to its higher melting point and smaller volume change at the monoclinic–tetragonal transition, the suppression of grain growth of HfO_2 nuclei by surrounding them with an Al_2O_3 matrix could contribute to the stabilization of the tetragonal phase at room temperature.

$m\text{-HfO}_2\text{--}\alpha\text{-Al}_2\text{O}_3$ and $m/t\text{-HfO}_2\text{--}\alpha\text{-Al}_2\text{O}_3$ nanocomposite films were prepared at 1573 K and 36–74 mol % Al_2O_3 . Fibrous microstructures of the $m/t\text{-HfO}_2$ dispersoids and the $\alpha\text{-Al}_2\text{O}_3$ matrix were observed at 59–74 mol % Al_2O_3 , which are near the eutectic composition of the $\text{HfO}_2\text{--}$

Al_2O_3 pseudo-binary system (67 mol % Al_2O_3). No melt formation was observed by SEM and TEM characterizations because the deposition temperature of 1573 K was lower than the eutectic temperature of the $\text{HfO}_2\text{--Al}_2\text{O}_3$ system (2163 K).

4. Conclusions

The $m\text{-HfO}_2\text{--}\alpha\text{-Al}_2\text{O}_3$ and $m/t\text{-HfO}_2\text{--}\alpha\text{-Al}_2\text{O}_3$ nanocomposite films were obtained at deposition temperatures of 1373–1573 K. The $t\text{-HfO}_2$ phase was also observed to be stabilized in an amorphous Al_2O_3 matrix for growth at 1323 K due to the suppression of HfO_2 grain growth by the surrounding matrix.

We observed that the $m\text{-HfO}_2\text{--}\alpha\text{-Al}_2\text{O}_3$ and $m/t\text{-HfO}_2\text{--}\alpha\text{-Al}_2\text{O}_3$ nanocomposite films with fibrous and lamellar grain structures at 1573 K and 36–74 mol % Al_2O_3 . Cross-sectional TEM characterization of the films prepared at 60 mol % Al_2O_3 revealed that the fibrous and lamellar $m/t\text{-HfO}_2$ dispersoids are present through the full thickness of the $\alpha\text{-Al}_2\text{O}_3$ columnar grains of the matrix. Because these nanocomposite films were formed around the eutectic composition of the $\text{HfO}_2\text{--Al}_2\text{O}_3$ pseudo-binary system (67 mol % Al_2O_3), the formation of fibrous and lamellar structures is associated with the eutectic nature of the system.

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