FULL PAPER

Precursor selection for metal–organic chemical vapor deposition of SrHfO₃ films with Sr(dpm)₂ and Sr(hfa)₂Sayaka FUJIE¹ and Akihiko ITO^{1,†}¹Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

SrHfO₃ films were prepared using metal–organic chemical vapor deposition (MOCVD) with hafnium tetrakis(acetylacetonate) and two different Sr precursors, and the effects of Sr content in the vapor and deposition temperature on crystal phase and microstructure were investigated. With the strontium bis(dipivaloylmethanate) [Sr(dpm)₂] precursor, low Sr content of the deposited films regardless of Sr supply ratio resulted in no detectable SrHfO₃ formation. With the strontium bis(hexafluoroacetylacetonate) [Sr(hfa)₂] precursor, along with linear increase of Sr content in the deposited films, the primary crystal phase of the film changed from monoclinic HfO₂ to orthorhombic SrHfO₃ to SrCO₃. A single-phase orthorhombic SrHfO₃ film was prepared with the Sr(hfa)₂ precursor at 1373 K and 42 mol % Sr (corresponding to 50 mol % Sr in the film).

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1. Introduction

Ceramic coatings protect a substrate from harsh environments with its excellent chemical stability and mechanical properties. Y₂O₃-stabilized ZrO₂ is widely used as a thermal barrier coating (TBC) for turbine blades in aircraft engines owing to its low thermal conductivity and high toughness.^{1)–3)} However, a new coating material suitable for the increased operating temperatures of gas turbine engines and a corresponding coating technique must be developed.

Perovskite-type zirconate and hafnate (AZrO₃ and AHfO₃; A = Ca, Sr, and Ba) are potential TBC materials due to low thermal conductivity, high melting points, and the wide possibility of site engineering in perovskite-type structures.^{4)–9)} Among them, SrHfO₃ is expected to exhibit a lower thermal conductivity (1.15 W m^{−1} K^{−1}) than YSZ (1.2–2.2 W m^{−1} K^{−1}) and comparable to those of SrZrO₃ (1.24) and BaHfO₃ (1.09),⁶⁾ and possesses a high melting point and comparable Vickers hardness (3200 K and 9.3 GPa)⁴⁾ as well as YSZ (2953 K and 11.8 GPa).¹⁰⁾

SrHfO₃ thin layers have been formed using atomic layer deposition^{11),12)} and molecular beam epitaxy^{13)–15)} as gate oxide onto Si and Ge wafers for semiconductor devices. These methods are not feasible for TBC because

deposition rates were extremely low, and post-annealing was required to obtain the crystalline phase of SrHfO₃. So far, literature includes no report on the preparation of SrHfO₃ thick films by TBC process, such as atmospheric pressure spray (APS) and electron-beam physical vapor deposition (EB-PVD) methods.

The present study aims to develop an SrHfO₃ coating process using metal–organic chemical vapor deposition (MOCVD) that can produce thick films of high-temperature structural ceramics at a relatively low processing temperature and high deposition rate. MOCVD provides excellent controllability of chemical composition and microstructure. We have demonstrated selective self-oriented growth of HfO₂ thick films having a columnar structure at a maximum deposition rate of 67 μm h^{−1}.^{16),17)} Therefore, MOCVD is a potential TBC process alternative to APS and EB-PVD.

Various precursor compounds are available for MOCVD. Not only deposition condition selection but also precursor selection is necessary to obtain the desired crystal phase and chemical composition. Luo et al. studied the synthesis of Sr-doped HfO₂ films via MOCVD using an amine compound; however, the obtained films were amorphous above 30 mol % Sr and no SrHfO₃ films were formed.¹⁸⁾ β-diketone compounds, such as dipivaloylmethanates and acetylacetonates, are widely used in MOCVD, and we prepared SrCO₃, SrTiO₃ and M-type SrFe₁₂O₁₉ films using strontium bis(dipivaloylmethanate) [Sr(dpm)₂].^{19)–21)} Strontium bis(hexafluoroacetylacetonate) [Sr(hfa)₂] was selected from the acetylacetonate group for comparison

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because strontium bis(acetylacetonate) contains water, which reduces the volatility of the precursor.

Here, we report MOCVD preparation of SrHfO₃ films with two different precursors of Sr(dpm)₂ and Sr(hfa)₂. The effects of the delivered precursor and its supply ratio on crystal phase and microstructure were studied.

2. Experimental procedure

The CVD apparatus has been described elsewhere.²²⁾ Metal–organic compounds of hafnium tetrakis(acetylacetonate) [Hf(acac)₄; Mitsuwa Chemicals, Japan], Sr(dpm)₂ (Toshima Manufacturing, Japan), and Sr(hfa)₂ (Strem Chemicals, USA) were maintained at temperatures of 413–513, 513–533, and 513–533 K, respectively, in precursor furnaces. The resultant vapor was transferred to the deposition chamber using Ar as a carrier gas, and O₂ gas was separately introduced into the chamber through a double-tube nozzle. The total chamber pressure was maintained at 200 Pa. The Sr content in the vapor was calculated from the mass change of each precursor.

A polycrystalline AlN plate (8 mm × 8 mm × 1 mm) was used as a substrate, because AlN is an accessible material with a high thermal shock resistance and thermal conductivity. A CO₂ laser (maximum power: 60 W) was used to irradiate the substrate through a ZnSe window, heating it to temperatures ranging from 863 to 1473 K. Deposition was performed for 0.6 ks. The deposition temperature was measured using an optical pyrometer.

The crystal phase of the resultant films was determined by X-ray diffraction (XRD; Bruker D2 Phaser) using Cu Kα radiation, generated at 30 kV and 10 mA. Cross-sectional and surface microstructure were observed using a scanning electron microscope (SEM; JEOL JCM-6000). An energy dispersive X-ray spectrometer integrated with the SEM (SEM-EDX; JEOL JSM-6510LA) and operated at an acceleration voltage of 20 kV was used to analyze film composition. SEM-EDX analysis was performed at 10 separate points on the film surface for each film sample. The crystal structures were schematically illustrated using the VESTA software package.²³⁾

The Harris texture coefficient (*TC*) was used to evaluate the degree of orientation.²⁴⁾

$$TC(hkl) = N \frac{I_m(hkl)/I_0(hkl)}{\sum I_m(HKL)/I_0(HKL)}, \quad (1)$$

where *N* is the number of peaks selected, and *I_m*(*hkl*) and *I_m*(*HKL*), and *I₀*(*hkl*) and *I₀*(*HKL*) are measured and reference intensities for *hkl* and *HKL* peaks in the XRD patterns, respectively. Planes of (011), (110), (11 $\bar{1}$), (111), (002), (020), (200), and (021) were used for the monoclinic HfO₂ (*m*-HfO₂; ICSD No. 27313) phase (*N* = 8), and planes of (020), (002), and (321) were used for the orthorhombic SrHfO₃ (*o*-SrHfO₃; ICSD No. 89383) phase (*N* = 3). *TC*(*hkl*) has a value between 0 and *N* depending on the degree of orientation, where the values of 1 and *N* indicate random and perfect orientations, respectively. The orientation degree [*OD*(*hkl*)] can be defined by the following formula when *TC*(*hkl*) > 1.

$$OD(hkl) = \frac{TC(hkl) - 1}{N - 1} \times 100 \quad (2)$$

3. Results and discussion

3.1 MOCVD with Sr(dpm)₂ precursor

Figure 1 shows typical XRD patterns of the films prepared with Sr(dpm)₂ precursor for various deposition temperatures and Sr content in the vapor. *m*-HfO₂ films were prepared with a significant (002) orientation with *OD*(002) = 88 % at 1473 K and 0 mol %Sr (without Sr supply) [Fig. 1(a)] and (020) orientation with *OD*(020) = 86 % at 1373 K and 15 mol %Sr [Fig. 1(b)]. A tetragonal HfO₂ (*t*-HfO₂; ICSD No. 173966) film was obtained at 1073 K and 67 mol %Sr [Fig. 1(c)].

Figure 2 summarizes the effect of the Sr content in the vapor and deposition temperature on the crystal phase of the films prepared with Sr(dpm)₂ precursor. Most of the films were *m*-HfO₂. Selective self-oriented growth was found in *m*-HfO₂ films, and *m*-HfO₂ films had significant (020) and (002) orientations for 15–30 and 30–40 mol %Sr, respectively. Films with a mixed-phase of *m*- and *t*-HfO₂ or single-phase *t*-HfO₂ films were obtained for a Sr content of the vapor exceeding 50 mol %. The SrHfO₃ phase was not formed under any deposition conditions. SEM-EDX analysis showed that Sr signals were undetectable in the films for any of the Sr contents in the vapor used in this study.

Possible reasons for the absence of Sr content in the films with the Sr(dpm)₂ precursor are: (1) gas-phase nucleation before reaching the substrate due to high evaporation and high deposition temperatures, (2) decreased reactivity on the substrate surface due to low evaporation and low deposition temperatures, and/or (3) decomposition of the

Fig. 1. XRD patterns of the (a) (002)-oriented *m*-HfO₂, (b) (020)-oriented *m*-HfO₂, and (c) *t*-HfO₂ films prepared with the Sr(dpm)₂ precursor at various deposition temperatures and Sr contents in the vapor: (a) 1473 K and 0 mol %Sr, (b) 1373 K and 15 mol %Sr, and (c) 1073 K and 67 mol %Sr.

Fig. 2. Effect of the Sr content in the vapor and deposition temperature on the crystal phase of the films prepared with the $\text{Sr}(\text{dpm})_2$ precursor.

Fig. 3. Cross-sectional SEM images of the (a) (002)- and (b) (020)-oriented $m\text{-HfO}_2$ film prepared with the $\text{Sr}(\text{dpm})_2$ precursor at various deposition temperatures and Sr contents in the vapor: (a) 1473 K and 0 mol %Sr, and (b) 1373 K and 15 mol %Sr.

films due to high deposition temperature. The current evaporation temperature for the $\text{Sr}(\text{dpm})_2$ precursor was 60 K lower than that of the previous study,¹⁹⁾ and no SrCO_3 or SrHfO_3 films were formed at any deposition temperature in the present study. We, therefore, deduce that the $\text{Sr}(\text{dpm})_2$ vapor had less reactivity on the film surface due to low evaporation temperature limited by the performance of the current precursor furnace.

The (002)-oriented $m\text{-HfO}_2$ films exhibited a columnar structure, as shown in Fig. 3(a), while most of the (020)-oriented films had a cone-like structure consisting of granular grains. This result was consistent with our previous study on self-oriented growth of $m\text{-HfO}_2$ films using

Fig. 4. Relationship between the Sr contents in the vapor and in the film prepared with the $\text{Sr}(\text{hfa})_2$ precursor.

MOCVD.¹⁶⁾ In ZrO_2 ^{25),26)} and HfO_2 ^{27),28)} nucleation from vapor has frequently been attributed to stabilization of the tetragonal phase over the monoclinic phase without any stabilizer elements. Both ZrO_2 and HfO_2 have a crystallographic relationship of $[010]_m \parallel [001]_t$ between their monoclinic and tetragonal structures, as shown in the insets of Figs. 1(b) and 1(c). Therefore, $m\text{-HfO}_2$ films composed of nanoparticles might favor the (020) orientation. On the other hand, in $m\text{-HfO}_2$ structure, an edge-sharing HfO_7 heptahedral chain is aligned along the c -axis, as illustrated in Fig. 1(a). This aspect of the crystal structure might preferentially form in a (002)-oriented growth for $m\text{-HfO}_2$ films accompanied with a columnar structure. In addition, according to Fig. 3(b), a (020)-oriented film with a columnar structure was obtained at 1373 K and 15 mol %Sr, which is in the boundary condition between (020) and (002) orientations. Deposition rates of the (002)- and (020)-oriented $m\text{-HfO}_2$ films were 77 and $37 \mu\text{m h}^{-1}$, respectively.

3.2 MOCVD with $\text{Sr}(\text{hfa})_2$ precursor

Figure 4 shows the relationship between Sr contents in the vapor and in the film prepared with the $\text{Sr}(\text{hfa})_2$ precursor. SEM-EDX analysis confirmed that the Sr content in the film increased linearly with the increase of that in the vapor, indicating that the Sr content in the film can be controlled by that in the vapor by changing the vaporization temperatures of each precursor.

Figure 5 shows XRD patterns of the films prepared with the $\text{Sr}(\text{hfa})_2$ precursor. $m\text{-HfO}_2$ film with a (020) orientation was obtained without Sr supply, and films with a mixed-phase of $m\text{-HfO}_2$ and $o\text{-SrHfO}_3$ film was obtained up to 40 mol %Sr. A single-phase $o\text{-SrHfO}_3$ film was prepared at 1373 K and 47 mol %Sr [Fig. 5(a)]. A SrCO_3 film with SrO and SrO_2 secondary phases was obtained at 1473 K and 100 mol %Sr [Fig. 5(b)].

Figure 6 summarizes the effect of the Sr content in the vapor and deposition temperature on the crystal phase of the films prepared with the $\text{Sr}(\text{hfa})_2$ precursor. The crystal

Fig. 5. XRD patterns of the (a) *o*-SrHfO₃ and (b) SrCO₃ films prepared with the Sr(hfa)₂ precursor at various deposition temperatures and Sr contents in the vapor: (a) 1373 K and 47 mol %Sr, and (b) 1473 K and 100 mol %Sr.

Fig. 6. Effect of the Sr content in the vapor and deposition temperature on the crystal phase of the films prepared with the Sr(hfa)₂ precursor.

phase changed from *m*-HfO₂ to *o*-SrHfO₃ to SrCO₃ with increasing Sr content in the vapor. Below a Sr content in the vapor of 40 mol %Sr, films with a mixed-phase of *m*/*t*-HfO₂ and SrHfO₃ were obtained. The single-phase *o*-SrHfO₃ film and the *o*-SrHfO₃ films with a minor amount of SrO and SrO₂ phases were obtained for Sr contents in the vapor of 40–75 mol %Sr.

Figure 7 shows the effect of the Sr content in the vapor on *a*- and *c*-axis lengths of the *o*-SrHfO₃ phase. Because the *b*-axis length showed almost the same trend as the *a*-axis length, only the *a*- and *c*-axis lengths are presented in the figure. The lattice parameters of the *o*-SrHfO₃ phase were close to the reference values (ICSD No. 89383;

Fig. 7. Effect of the Sr content in the vapor on (a) *a*- and (b) *c*-axis lengths of the *o*-SrHfO₃ phase in the films.

Fig. 8. (a) Cross-sectional and (b) surface SEM images of the single-phase *o*-SrHfO₃ films prepared with the Sr(hfa)₂ precursor at 1373 K and 42 mol %Sr.

$a_{\text{ref}} = 0.5752$ nm, $b_{\text{ref}} = 0.5765$ nm, $c_{\text{ref}} = 0.8134$ nm) and almost constant for 15–42 mol %Sr. The lattice parameters decreased to ($a = 0.5723$ nm, $b = 0.5723$ nm, $c = 0.8096$ nm) with increasing Sr content up to 70 mol %Sr. Figure 8 shows the typical cross-sectional and surface SEM images of single-phase *o*-SrHfO₃ prepared at 1373 K and 47 mol %Sr. The *o*-SrHfO₃ films had a solid structure in cross-section covered with a faceted surface, and the deposition rate was 6 μm h^{−1}.

The *o*-SrHfO₃ phase was formed with the *m*-HfO₂ phase by the Sr(hfa)₂ precursor supplied at 15–42 mol %Sr. The lattice parameters of the *o*-SrHfO₃ phase remained close to the reference value below 42 mol %Sr, suggesting that the

stoichiometric *o*-SrHfO₃ phase was readily formed below 42 mol %Sr. The amount of SrO and SrO₂ phases formed increased with increasing Sr content in the vapor above 42 mol %Sr, and the lattice parameters of the *o*-SrHfO₃ phase decreased. These results suggest that the Sr-deficient *o*-SrHfO₃ phase was formed above 42 mol %Sr because SrO and SrO₂ phases were formed preferentially. The synthesis window for the single-phase stoichiometric *o*-SrHfO₃ phase is 1373 K and 42 mol %Sr in the vapor (corresponding to 50 mol %Sr in the film).

4. Conclusions

SrHfO₃ films were prepared using MOCVD using two different Sr precursors, and the results of the present study can be summarized as follows.

- With the Sr(dpm)₂ precursor, elemental Sr was undetectable in the deposited film; thus, no SrHfO₃ phase was formed. However, a small addition of Sr content may help self-oriented growth with (020) and (002) orientations of *m*-HfO₂ phase, and stabilization of the *t*-HfO₂ phase.
- With the Sr(hfa)₂ precursor, the crystal phase of the deposited films changed from *m*-HfO₂ to *o*-SrHfO₃ to SrCO₃ with linear increase of the Sr content in the vapor. The lattice parameters of the *o*-SrHfO₃ phase were constant in the HfO₂-SrHfO₃ films, while they decreased with increase of Sr content above 42 mol %Sr due to the formation of SrO and SrO₂ phases, possibly accompanied by Sr deficiency in the *o*-SrHfO₃ phase. The single-phase *o*-SrHfO₃ film was prepared at 1373 K and 42 mol %Sr in the vapor (corresponding to 50 mol %Sr in the film) at the high deposition rate of 6 μm h⁻¹.

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