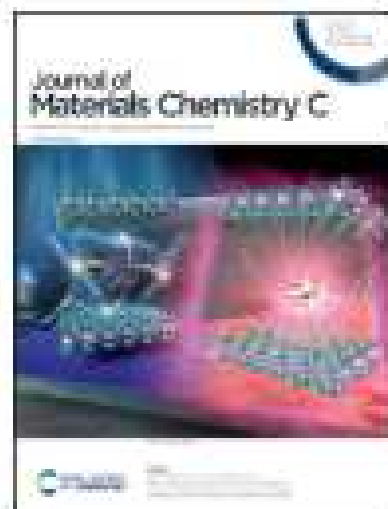


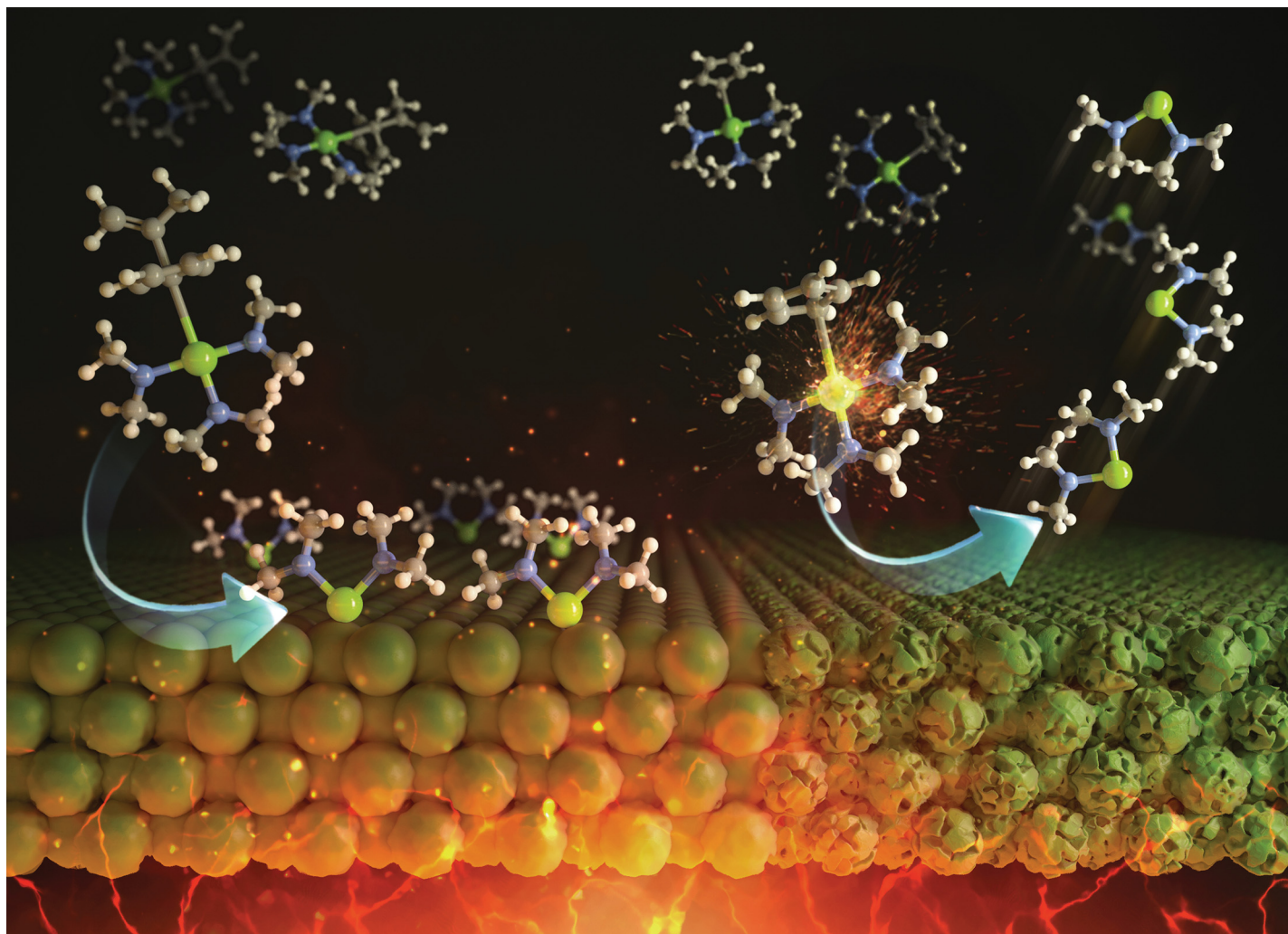
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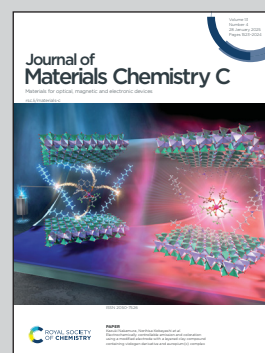


Showcasing research from Professor Tae Joo Park's laboratory, Department of Materials Science and Chemical Engineering, Hanyang University, Ansan, Republic of Korea.

High-temperature atomic layer deposition of HfO_2 film with low impurity using a novel Hf precursor

HfO_2 film was grown using a novel Hf precursor, $\text{FuHf}(\text{NMe}_2)_3$. Physicochemical and electrical properties were improved at high temperature compared to film grown using the $\text{CpHf}(\text{NMe}_2)_3$ precursor, and it was verified by theoretical calculations.

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High-temperature atomic layer deposition of HfO₂ film with low impurity using a novel Hf precursor†

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We compared the physicochemical and electrical properties of HfO₂ thin films grown at a high temperature of 350 °C using tris(dimethylamido)cyclopentadienylhafnium (CpHf(NMe₂)₃) and a novel Hf precursor, tris(dimethylamido)isopropenylcyclopentadienylhafnium (FuHf(NMe₂)₃). Experimental results indicate that the FuHf(NMe₂)₃ precursor exhibits superior thermal stability compared to the CpHf(NMe₂)₃ precursor, making it highly advantageous for high-temperature processes. Accordingly, the ALD temperature window range of the film grown using FuHf(NMe₂)₃ is higher by approximately 50 °C. Due to the enhanced thermal stability, the HfO₂ film grown using FuHf(NMe₂)₃ exhibits reduced impurity concentration compared to the film grown using CpHf(NMe₂)₃, resulting in increased physical density. Consequently, the improved physicochemical properties of HfO₂ films grown using FuHf(NMe₂)₃ enhanced their electrical characteristics including dielectric constant, leakage current, and dielectric breakdown properties.

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1. Introduction

Atomic layer deposition (ALD) is a thin film growth technique based on surface reaction mechanism chemisorption of precursor molecules.^{1–5} Therefore, ALD offers advantages in fabricating devices with complex structures, allowing precise control of film thickness at the atomic layer level, ensuring excellent conformality, and enabling detailed control of film composition. The selection of the precursor is crucial as it significantly influences the physicochemical properties of the resultant thin film.⁶

HfO₂ film has been widely employed in diverse electronic devices due to its high dielectric constant, wide band gap energy, excellent thermal stability, and strong compatibility with Si.^{7–14} Given the stringent requirements for dielectric films in next-generation electronic devices, which need high levels of insulation and reliability, employing a high-temperature process for producing high-quality HfO₂ that meets these criteria becomes imperative. Consequently, the use of precursors with superior thermal stability, reactivity, and minimal byproduct

contamination becomes crucial. This approach enables the growth of denser films with fewer impurities and defects.^{15,16} Furthermore, by expanding the ALD temperature window, various other ALD processes can be employed, enhancing the overall performance of the film. In general, HfO₂ films grown using homoleptic Hf alkyl amide precursors, such as tetrakis(dimethylamido)hafnium (TDMAHf) and tetrakis(diethylamido)hafnium (TDEAHf) exhibit excellent physicochemical properties and conformality at temperatures below 300 °C. However, at higher temperatures, the thermal decomposition of these precursors leads to increased impurity concentrations, decreased physical density, deteriorated uniformity and conformality of the film.^{17–19} The Hf alkoxide precursor demonstrates superior thermal stability compared to the Hf alkyl amide precursor; however, achieving ALD growth behavior is challenging due to the non-saturated growth characteristics resulting from β -hydride elimination reaction.^{20–22} The Hf halide precursor, HfCl₄ exhibits excellent thermal stability and is suitable for high-temperature process. Nonetheless, the corrosive nature of the HCl byproduct gas generated during the ALD reaction adversely affects film growth behavior.^{23–26} The tris(dimethylamido)cyclopentadienylhafnium (CpHf(NMe₂)₃, or CpHf) precursor, a recently employed heteroleptic precursor with a Cp ligand replacing a ligand of the TDMAHf precursor, exhibits desirable characteristics such as volatility, reactivity, and exceptional thermal stability, providing significant advantages for high-temperature processes. However, the thermal stability of the precursor is limited as thermal decomposition occurs at temperatures above 350 °C.^{27,28}

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To address this issue in this study, we introduce a novel Hf precursor, tris(dimethylamido)isopropenylcyclopentadienylhafnium ($\text{FuHf}(\text{NMe}_2)_3$, or FuHf), which is a heteroleptic precursor with exceptional thermal stability, reported here for the first time. We compared the growth behavior, physicochemical characteristics, and electrical properties of HfO_2 films grown using the CpHf and FuHf precursors at a high temperature of 350°C .

2. Experimental

2.1. Precursor synthesis

In a flame-dried 500 mL Schlenk flask, TDMAHf (50 g, 0.14 mol) was added to anhydrous hexane (200 mL) and stirred at 0°C . To this solution, 6,6-dimethylfulvene (18 g, 0.17 mol) was slowly added while maintaining the temperature at 0 – 5°C . Subsequently, the reaction mixture was gradually warmed to room temperature and stirred for 24 hours. After the reaction, the solvent was removed under reduced pressure, and the product was distilled under vacuum to obtain tris(dimethylamido)isopropenylcyclopentadienylhafnium with a yield of 95%.²⁹ The complex was characterized by nuclear magnetic resonance (NMR) as shown in Fig. S1 (ESI[†]).

2.2. ALD HfO_2

Boron-doped p-type Si (100) substrates with a resistivity of 10 – $12\ \Omega\ \text{cm}$ were cleaned in a dilute hydrofluoric acid solution ($\sim 10\%$) to eliminate any native oxide and then rinsed in deionized water. Then, ALD HfO_2 films were grown on the cleaned Si substrates at 350°C in a 4-inch traveling wave-type thermal ALD reactor. CpHf and FuHf were used as Hf precursors, and O_3 ($180\ \text{g}\ \text{m}^{-3}$) was used as an oxygen source. High-purity N_2 (99.999%) was used as a carrier and purge gas with a flow rate of 200 standard cubic centimeters per minute. The pulse and purge times of Hf precursors and O_3 required to achieve the self-limited growth characteristics are determined in Fig. S2 (ESI[†]).

2.3. Physicochemical analysis

Film thickness was measured using *ex situ* spectroscopic ellipsometry (SE, MG-1000, Nanoview Co.) with a spectral range of 380 – $900\ \text{nm}$ at a fixed incidence light angle of 70° . The layer density was measured using energy dispersive X-ray fluorescence (EDXRF, ARL Quant'X, Thermo Fisher Scientific Co.). The physical density of films was examined using X-ray reflectometry (XRR, ATX-G, Rigaku Co.). The crystallinity of films was estimated by X-ray diffraction (XRD, Smartlab, Rigaku Co.) in the glancing incidence (GI) mode with a 1° incidence angle using $\text{Cu}\ \text{K}\alpha$ radiation. The microstructures of the films were observed using a high resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL) operating at $200\ \text{kV}$ in the bright-field imaging mode. The chemical binding states of films were examined using X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific Co.) with an $\text{Al}\ \text{K}\alpha$ monochromatic source of $1486.6\ \text{eV}$. Binding energy of the XPS

spectra was calibrated using the Si 2p (Si–Si bonding, $99.6\ \text{eV}$) peak. Elemental depth profiles were obtained using Auger electron spectroscopy (AES, PHI-700 Xi, Physical Electronics) with an electron beam energy of $0.5\ \text{keV}$ and time-of-flight secondary ion mass spectrometry (ToF-SIMS, TOF.SIMS 5, ION-TOF) with a $30\ \text{keV}\ \text{Bi}^+$ ion gun ($50 \times 50\ \mu\text{m}^2$).

2.4. Electrical characterizations

Metal-oxide-semiconductor (MOS) capacitors were fabricated with $100\ \text{nm}$ -thick TiN top electrodes deposited through a shadow mask *via* DC magnetron sputtering. The capacitors underwent forming gas ($5\%\ \text{H}_2$ balanced with Ar) annealing at 400°C for 30 min. Then, an In–Ga eutectic alloy was employed to establish a backside ohmic contact. Capacitance–voltage (C – V) and current density–voltage (J_g – V) characteristics of the MOS devices were assessed using a semiconductor parameter analyzer system (4200-SCS, Keithley). Capacitance equivalent thickness (CET) values were calculated based on the accumulation capacitance measured at a frequency of $1\ \text{MHz}$.

2.5. Computational details

Theoretical calculations were performed using a universal interatomic machine-learning potential (MLP), namely Preferred Potential (PFP) within the Matlantis software package (Preferred Computational Chemistry, Inc.).^{30,31} Previous results show MLP calculations using PFP could accurately capture the ALD surface chemistry of Al_2O_3 .³² All geometry optimizations using PFP were conducted using LBFGS algorithm with maximum remaining force of $0.001\ \text{eV}\ \text{\AA}^{-1}$. To calculate the transition state, climbing-image nudged elastic band (CI-NEB) method³³ with maximum remaining force of $0.02\ \text{eV}\ \text{\AA}^{-1}$ was used. Slab model of the monoclinic HfO_2 (001) surface with a hydration coverage of $1.3\ \text{H}_2\text{O}$ molecules per nm^2 was used, which is known for thermodynamic stable form of (001) monoclinic HfO_2 at the temperature of 350°C ,³⁴ as shown in Fig. S3 (ESI[†]). The slab dimensions (length $\times$ width $\times$ height) were ($15.36 \times 15.53 \times 40.69$) $\text{\AA}^3$, incorporating 90 hafnium, 183 oxygen, and 6 hydrogen atoms. To reduce any unphysical interactions between slabs, vacuum space of $27\ \text{\AA}$ in the vertical direction was maintained. The slab consisted of five layers of HfO_2 , whose lower three layers was fixed, while the top two layers and adsorbates were allowed to relax during optimization. The adsorption energy (E_{ad}) and activation energy (E_{a}) are defined using following equations:

$$E_{\text{ad}} = E_{\text{adduct}} - (E_{\text{slab}} + E_{\text{precursor}}) + E_{\text{byproduct}}$$

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{ad}}$$

where E_{adduct} , E_{slab} , $E_{\text{precursor}}$, $E_{\text{byproduct}}$, and E_{TS} indicate the energy of slab with the adduct, clean slab, gaseous precursor, gaseous byproduct, and transition state, respectively. The surface-projected areas of the adsorbed precursors were calculated using Chemcraft 1.8 software package.

Density functional theory (DFT) calculations were performed using Vienna ab initio simulation package (VASP) version 6.3.2.³⁵ For DFT calculations, a slab consisted of three layers of HfO_2 was used, created by removing the bottom two layers

from the slab model used in the MLP calculations. The bottom-most layer of the slab was fixed, while the top two layers and the adsorbates were allowed to relax during optimization. The Perdew–Burke–Ernzerhof (PBE) functional³⁶ based on generalized gradient approximation (GGA) was employed with D3 (BJ) correction for dispersion.³⁷ The projector augmented wave (PAW) method³⁸ was employed with a cutoff energy of 450 eV and Monkhorst–Pack k -point mesh of $4 \times 4 \times 1$. The convergence criteria for energy and force were set to 10^{-5} eV and $0.05 \text{ eV } \text{\AA}^{-1}$, respectively. Additionally, to compare the DFT results with MLP, the optimized structures obtained from DFT were re-calculated using MLP.

3. Results and discussion

Fig. 1a illustrates the molecular structures of CpHf and FuHf precursors. FuHf is a variant where the Cp ligand of CpHf is substituted with a modified Cp-based ligand. FuHf is larger in size than CpHf and exhibits an asymmetric molecular structure. Fig. 1b shows the Hf layer density and thickness of the films (50 ALD cycles) grown using the two precursors as a function of growth temperature; density and thickness were measured by EDXRF and SE, respectively. The Hf layer density

and thickness of the film grown using CpHf increased substantially at temperatures over 350°C , indicating the thermal decomposition of the precursor. However, the Hf layer density and thickness of the film grown using FuHf were stable up to 400°C , which suggests that FuHf offers superior thermal stability compared to CpHf, making it an advantageous choice for higher temperature processes.

The surface reactions of the Hf precursors were investigated using MLP calculations. First, the dissociative adsorption reactions of the precursors on the HfO_2 surface are considered. As the activation energy (E_a) for removal of Cp-type ligands from precursors is significantly greater than that for the amido ligands (Fig. S4a and b, ESI†), it can be confirmed that Cp-type ligands would preferentially remain on the surface after adsorption of the precursors.^{39–41} Furthermore, while removal of the first amido ligands are highly exothermic and involve small E_a values, E_a increases and reaction energy becomes endothermic as more ligands are removed from the precursor (Fig. S4c, ESI†). In this regard, both precursors exhibit similar energy changes during adsorption on the surface. Thus, the adsorption structures including one Cp-type and one amido ligands remaining on the Hf atom can be expected to occur. Current MLP calculation results on the adsorption energy of several possible configurations for both of the precursors are in good

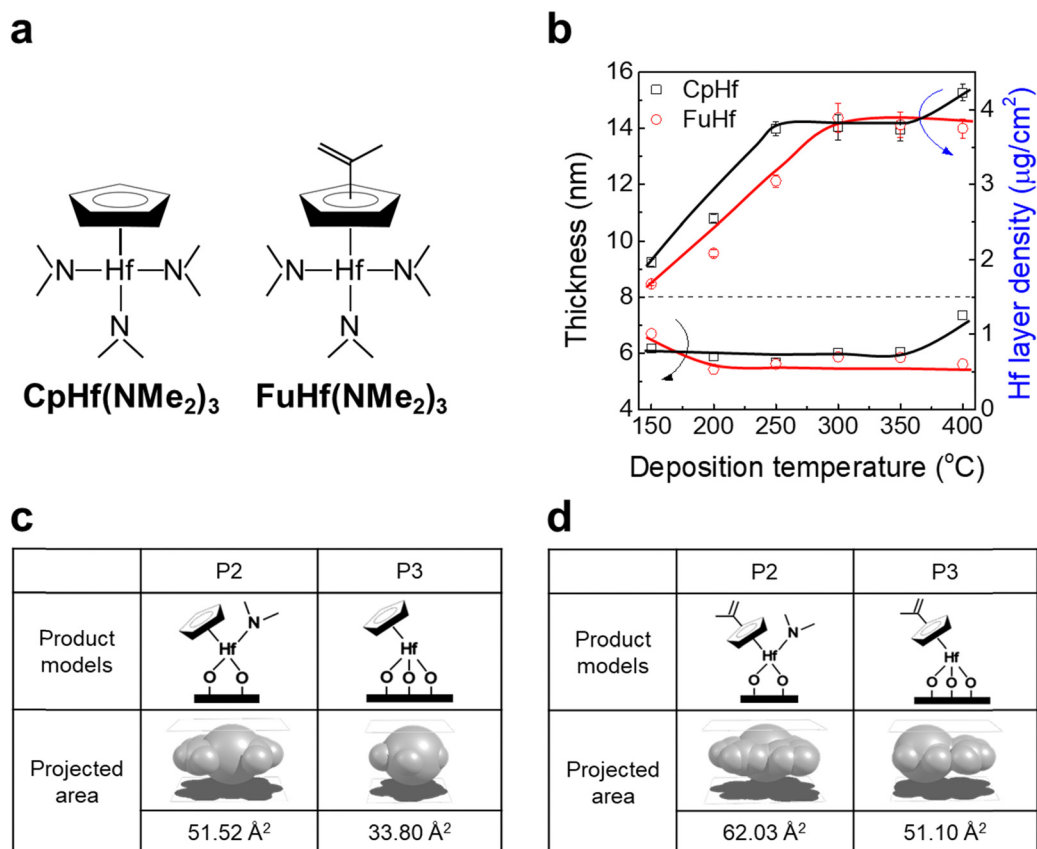


Fig. 1 (a) The molecular structures of $\text{CpHf}(\text{NMe}_2)_3$ and $\text{FuHf}(\text{NMe}_2)_3$ precursors. (b) Film thickness and Hf layer density of ALD HfO_2 thin films grown using $\text{CpHf}(\text{NMe}_2)_3$ and $\text{FuHf}(\text{NMe}_2)_3$ precursors as a function of growth temperature. Projected areas of the adsorption products of (c) CpHf and (d) FuHf on the HfO_2 surface. P_n = chemisorption product after removal of n byproducts.

agreement with the DFT results, verifying the reliability of the MLP method (Fig. S5a and b, ESI†).

Additionally, the impact of the precursors' structure on growth rate was evaluated by calculating the size of the surface-adsorbed precursors. Fig. 1c and d show the occupied surface areas per possible structures formed from the adsorption of CpHf and FuHf precursors. Here, the occupied area was calculated as the area of the orthographic projection of each adsorption structure's van der Waals volume onto the surface plane. P2 and P3 represent the structures of adsorbates with

2 and 3 amido ligands dissociated, respectively. Comparing the surface area per adsorbed Hf atom in P2 and P3 structures, it is evident that FuHf occupies a larger area in both structures. As a result, it is predicted that the steric hindrance effect of FuHf is greater than that of CpHf, resulting in smaller adsorption density and growth rate.^{42,43}

We compared the physical properties of HfO₂ films grown using the CpHf and FuHf precursors. The growth temperature of the films was 350 °C, which is the highest within the overlapped temperature window for ALD growth using the

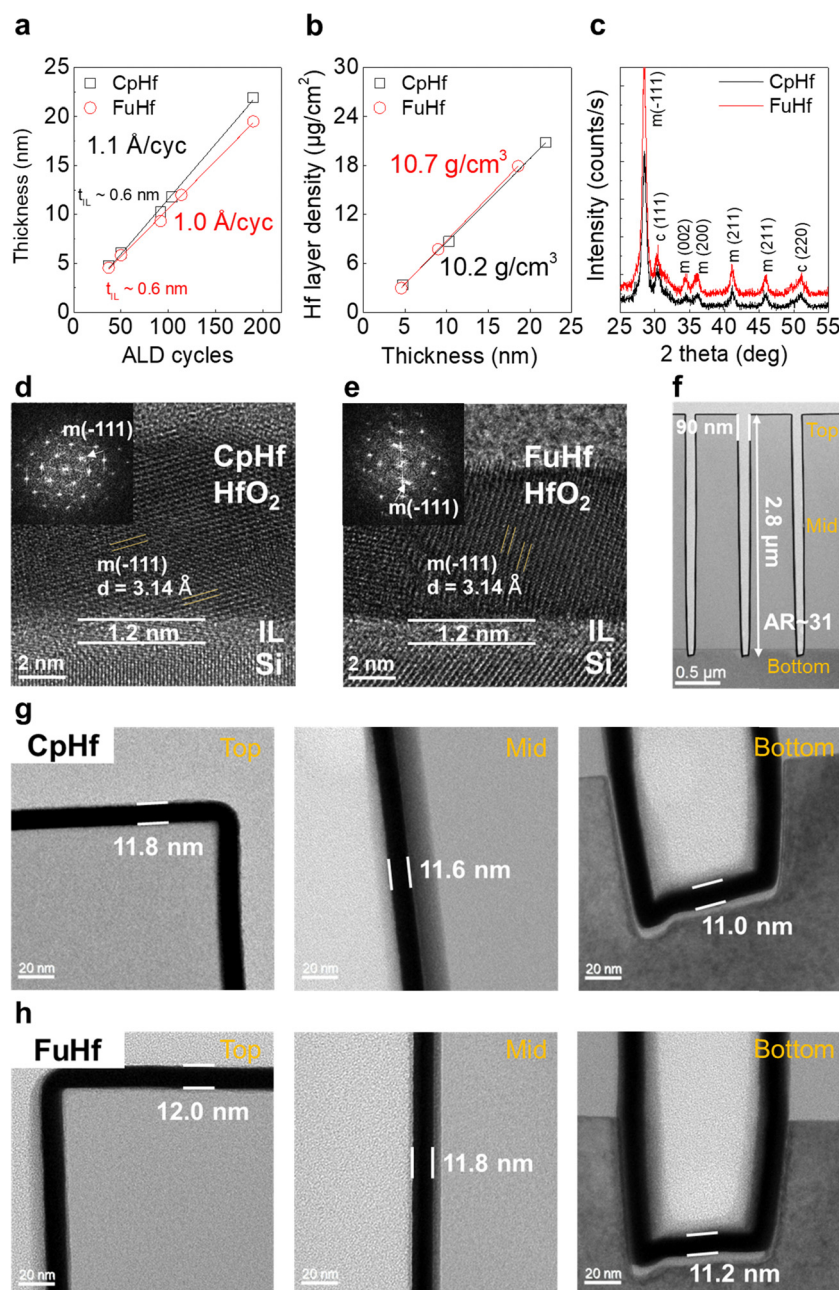


Fig. 2 (a) HfO₂ film thickness as a function of number of ALD cycles, (b) Hf layer density as a function of film thickness. (c) GIXRD patterns of 20 nm-thick HfO₂ films. Cross-sectional HRTEM images of HfO₂ films grown using (d) CpHf(NMe₂)₃ and (e) FuHf(NMe₂)₃ precursor with selected area electron diffraction pattern. Cross-sectional TEM images of (f) Si deep trench substrate and (g) and (h) HfO₂ films grown using CpHf(NMe₂)₃ and FuHf(NMe₂)₃ precursors, respectively, at the top, mid and bottom region of Si trench.

two precursors (see Fig. 1b). Fig. 2a shows the thickness of HfO_2 films measured by SE as a function of the number of ALD cycles. The growth rates of HfO_2 films grown using CpHf and FuHf were determined to be 1.1 and 1.0 Å per cycle, respectively. The slightly lower growth rate of the film grown using FuHf is attributed to the larger steric hindrance effect resulting from the larger modified Cp ligand of FuHf.^{44,45} The calculated thickness of the interfacial layer (IL) was similar, approximately ~0.6 nm for both cases. The Hf layer densities of the films measured using EDXRF as a function of film thickness are presented in Fig. 2b. The physical densities calculated from the slopes of the curves is 10.7 g cm⁻³ for FuHf, larger than 10.2 g cm⁻³ for CpHf. The physical densities of films were confirmed through XRR analysis (Fig. S6, ESI†), which were 10.3 and 10.2 g cm⁻³ for FuHf and CpHf, respectively. The higher density of the HfO_2 film grown using FuHf can be attributed to its lower residual impurity concentration, resulting from suppressed residual ligand incorporation at such a high growth temperature, facilitated by the enhanced thermal stability characteristics of FuHf. These characteristics make it difficult for additional precursor molecules to be adsorbed after the initial reaction, thereby preventing further incorporation of ligand residues into the film, which is discussed in detail later.

To assess the crystallinity of the HfO_2 films, GIXRD analysis was conducted on 20 nm-thick films as illustrated in Fig. 2c. Both monoclinic and cubic phases were observed, irrespective of the precursor type,^{21,27,45–47} however, the HfO_2 film grown using FuHf exhibited the higher intensity, indicating superior crystallinity compared to the film grown using CpHf. Fig. 2d and e show the microstructures of the HfO_2 films observed by

cross-sectional HRTEM. The IL thicknesses of the two films are similar, approximately ~1.2 nm, which is consistent with the result in Fig. 2a. The selected area electron diffraction pattern and interplanar spacing values ($d = 3.14$ Å) confirmed the presence of the monoclinic (–111) crystal structure in both HfO_2 films, which is consistent with the GIXRD results. The step coverage of the HfO_2 films was estimated and compared at the top, mid and bottom region of the deep trench structure with an aspect ratio of ~31 (90 nm-opening and 2.8 μm-depth) in Si substrate as shown in the cross-sectional TEM image of Fig. 2f. The number of cycles for each precursor was adjusted based on the growth rate to achieve films of similar thickness (~12 nm). As a result, 104 and 114 cycles were used for the CpHf precursor and FuHf precursor, respectively. The thickness of HfO_2 film grown using CpHf is ~11.8, ~11.6 and ~11.0 nm at the top, mid and bottom region, respectively (Fig. 2g). Similarly, the thickness of HfO_2 film grown using FuHf is ~12.0, ~11.8 and ~11.2 nm at the top, mid and bottom region, respectively (Fig. 2h). The average step coverage values of the two films are high and similar, ~94%, suggesting its suitability for 3-dimensional semiconductor device structures.^{10,48}

The chemical binding states of the HfO_2 films were examined using XPS. Fig. 3a and b show the Hf 4f and O 1s core level spectra of 20 nm-thick HfO_2 films grown using CpHf and FuHf, respectively. The Hf 4f spectra exhibited no noticeable difference associated with the type of precursor used, which suggests the identical chemical structure of HfO_2 films. This was supported by identical O 1s core level spectra of the two films.¹⁹ Furthermore, to verify the chemical binding states at the interface between HfO_2 film and Si substrate, 4 nm-thick HfO_2 films

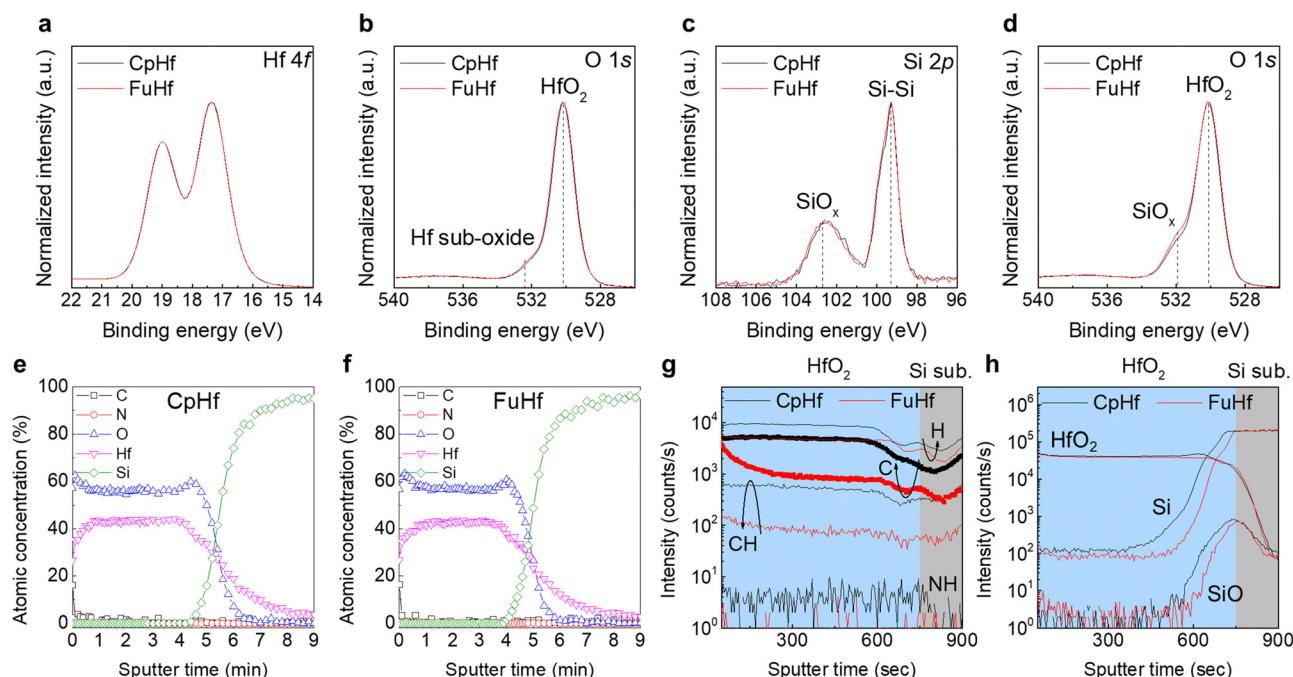


Fig. 3 (a) Hf 4f and (b) O 1s core level XPS spectra of 20 nm-thick HfO_2 films (c) Si 2p, (d) O 1s core level XPS spectra of 4 nm-thick HfO_2 films grown using CpHf(NMe_2)₃ and FuHf(NMe_2)₃ precursor. AES depth profile of HfO_2 films grown using (e) CpHf(NMe_2)₃ and (f) FuHf(NMe_2)₃ precursor. SIMS depth profiles of (g) the impurities and (h) diffused Si in HfO_2 films grown using CpHf(NMe_2)₃ and FuHf(NMe_2)₃ precursor.

were also used for XPS analysis. The Si 2p and O 1s core level spectra of the films presented in Fig. 3c and d, respectively, are almost identical including the SiO_x peaks corresponding to the IL formed during the ALD process,^{49–57} which is consistent with HRTEM results in Fig. 2d and e.

The chemical composition and impurity concentration in the HfO_2 films were observed by AES depth profile as shown in Fig. 3e and f. In both HfO_2 films uniform chemical composition of Hf and O was observed with consistent levels of major impurities such as C and N, both at approximately 1%, except for the surface carbonaceous contamination. To examine precisely the impurities level present in the films, we conducted ToF-SIMS depth profile analysis as shown in Fig. 3g and h. Fig. 3g presents the depth profile of major impurities including H, C, CH and NH, which may originate from the ligand residue of the precursor molecule during the ALD reaction. The signal intensities of all the impurities were lower by approximately half to an order of magnitude for the HfO_2 film grown using FuHf compared to the film grown using CpHf. This reduction is attributed to the suppressed incorporation of ligand residues facilitated by the enhanced thermal stability of FuHf as previously mentioned, resulting in a higher film density.¹⁹ Fig. 3h shows the ToF-SIMS depth profile of HfO_2 , Si, and Si, where the

HfO_2 signal intensities of the two films are almost identical, suggesting that the film thicknesses are the same. However, there was a noticeable difference in Si and SiO signal intensities. Considering the identical IL thickness according to TEM analysis results (Fig. 2d and e), the Si diffusion into the HfO_2 film during ALD was suppressed for the film grown using FuHf compared to the film grown using CpHf, which is attributed to its higher film density.

MOS capacitors were fabricated using the 10 nm-thick HfO_2 films with TiN top electrode, and their electrical characteristics were compared. Fig. 4a presents the typical $C-V$ curves of the MOS capacitors. It is noteworthy that the accumulation capacitance density of the film grown using FuHf was larger than that of the film grown using CpHf. The hysteresis values were significantly low, less than 25 mV, regardless of precursor type. Fig. 4b shows the CET as a function of HfO_2 film thickness, which was calculated based on the accumulation capacitance obtained from the $C-V$ curves of the capacitors with 4, 10, and 20 nm-thick HfO_2 films (Fig. S7, ESI†). The dielectric constants were calculated using the slope of the curves, which were 15.8 and 14.6 for the films grown using FuHf and CpHf, respectively. The larger dielectric constant of the film grown using FuHf is attributed to the higher physical density of the HfO_2 film with

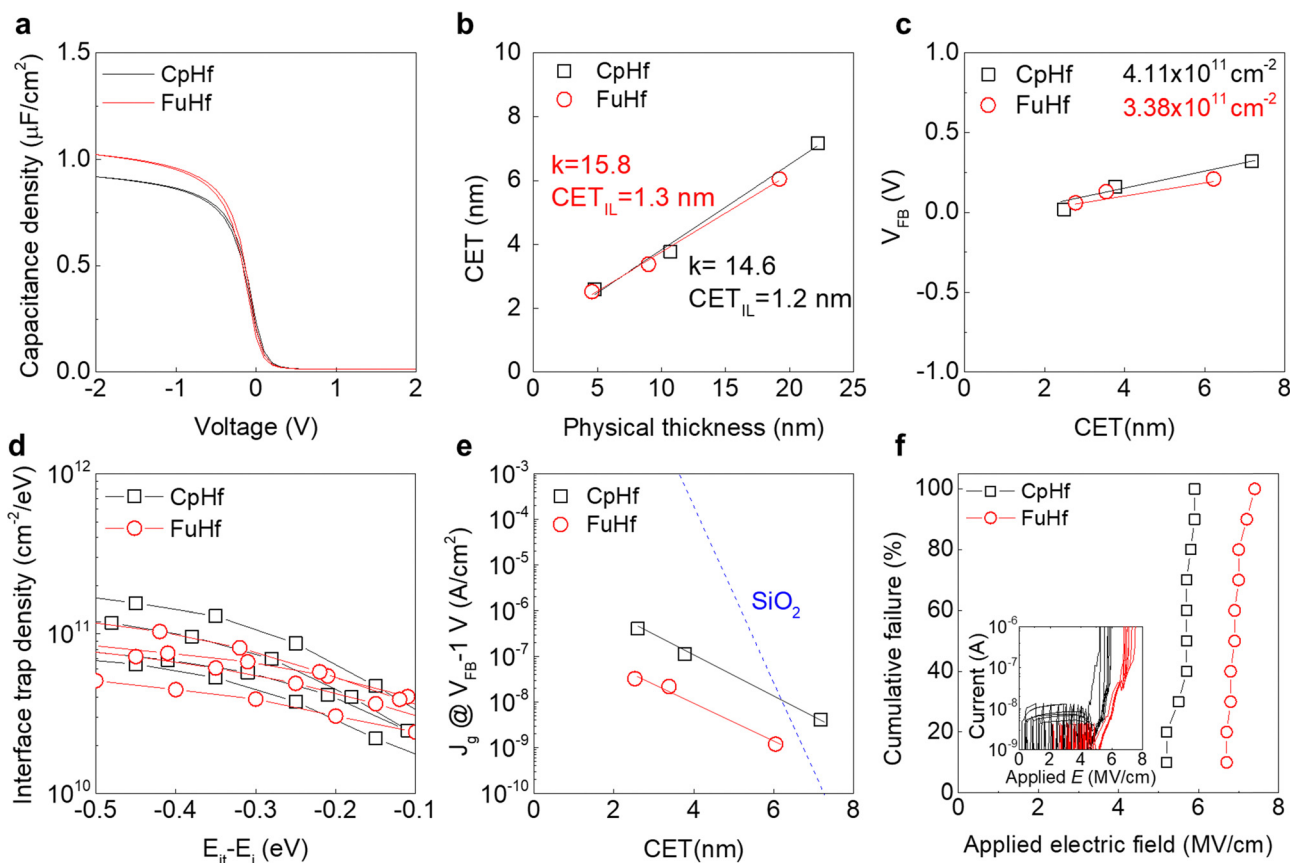


Fig. 4 (a) Typical capacitance–voltage curves for the MOS capacitors. (b) CET as a function of film thickness and (c) V_{FB} as a function of CET for the HfO_2 film grown using the CpHf(NMe_2)₃ and FuHf(NMe_2)₃. (d) Interface state density (D_{it}) measured using conductance method as a function of the energy level in Si band gap. (e) Plots of J_{g} vs. CET and (f) time-zero dielectric-breakdown (TZDB) of the MOS capacitors with the HfO_2 films grown using CpHf (NMe_2)₃ and FuHf(NMe_2)₃.

low impurity concentration compared to the film grown using CpHf. The calculated CET of the IL was confirmed to be at a similar level of $\sim 1.2\text{--}1.3$ nm, consistent with the results of SE, XPS, and cross-sectional TEM results above. Fig. 4c shows the flatband voltage (V_{FB}) as a function of CET of HfO_2 films, where the fixed charge density was calculated using the slope of the curve. The fixed charge density of the film grown using FuHf ($3.38 \times 10^{11} \text{ cm}^{-2}$) was slightly lower than that of the film grown using CpHf ($4.11 \times 10^{11} \text{ cm}^{-2}$).⁵⁸ The interface state densities (D_{it}) within the Si energy band gap of several MOS capacitors were measured using the conductance method as shown in Fig. 4d, confirming that FuHf improved the interface property.^{58–62}

The plot of J_g vs. CET in Fig. 4e shows that the HfO_2 film grown using FuHf exhibited an order of magnitude lower J_g at all CET ranges compared to the film grown with CpHf. The simulation results of the SiO_2 film were also included for comparison.⁶³ Furthermore, to assess the reliability of the device, the time-zero dielectric breakdown (TZDB) characteristics were estimated. The cumulative failure results are depicted in Fig. 4f and the leakage current–electric field (I – E) curves are presented in the inset figure. The average breakdown fields of the HfO_2 films grown using CpHf and FuHf were 5.9 and 7.0 MV cm^{-1} , respectively. These improvements of reliabilities are primarily attributable to the improved physicochemical properties of HfO_2 films grown using FuHf.^{59,64–66}

4. Conclusions

We compared the physicochemical and electrical properties of HfO_2 films grown using a CpHf precursor and a novel Hf precursor, FuHf at a high temperature of 350 °C. The FuHf precursor has a bulkier ligand compared to the CpHf precursor, resulting in a slightly reduced growth rate due to steric hindrance. However, the ALD temperature window of the film grown using FuHf demonstrated its superior stability for high temperature processes compared to CpHf. Therefore, HfO_2 films grown using the FuHf precursor exhibited the higher film density and the lower impurity concentrations compared to those grown using CpHf precursor. As a result, various electrical properties including the dielectric constant, fixed charge density, interface state density, gate leakage current, and dielectric breakdown characteristics were significantly improved in FuHf-grown films. HfO_2 films grown using the FuHf precursor also exhibited good step coverage in high aspect ratio structures, showing promise for practical integration into next-generation semiconductors with complex architectures.

Author contributions

J. C. P. and C. I. C. conceived the study, carried out the experiments and characterizations and wrote the manuscript. W. P. J., T. T. N. V., and B. S. performed the theoretical studies and collected the data. W.-H. K. and J.-H. A. contributed to the

characterization of the samples. B. S. and T. J. P. contributed to revising the manuscript. T. J. P. conceived the original ideas and supervised the project. All authors have given approval to the final version of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.† Further information and data are available upon request from the authors.

Conflicts of interest

There are no conflicts of interest to declare.

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