

Supporting information

Novel halogenated cyclopentadienyl hafnium precursor for atomic layer deposition of high-performance HfO₂ thin film

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Experimental

Material and Chemicals

All reagents were used as received without further purification. 2.5M n-BuLi in hexane, n-pentane (anhydrous, 99%) and iodine (99%) were purchased from Sigma-Aldrich. Tetrakis(dimethylamido)hafnium(IV) (99.99%) was purchased from EM Chemicals. Dicyclopentadiene (97%) was purchased from Tokyo Chemical Industry (TCI). ¹H nuclear magnetic resonance (NMR) spectra were recorded on a JNM-ECZ400S/L1 spectrometer. High-performance liquid chromatography (HPLC) was carried out using a Shimadzu Nexera UHPLC.

Synthesis

Lithium-cyclopentadienide (1)

Cyclopentadiene (2.0 g, 30.26 mmol, 1.5 eq) was placed into a 100 mL 1-neck round flask, followed by the addition of 30 mL of anhydrous pentane at 0°C in an ice bath, and stirred for 30 minutes. Then, 2.5M n-BuLi solution in hexane (8.22 mL, 20.55 mmol, 1.0 eq) was slowly added dropwise over one hour. During the addition, the clear and transparent solution turned into an opaque white substance. After completion of the addition, the ice bath was removed, and stirring was continued for an additional 30 minutes at room temperature to confirm the slushy state formation. Vacuum filtration was performed 2-3 times using a small amount of

anhydrous pentane. After filtration, a white powder substance was obtained (yield: 1.5 g, 68.8%). ^1H NMR (DMSO-d_6): δ 5.32 (s, 5H).

5-iodocyclopentadiene (2)

In a glove box, compound (1) (0.39 g, 5.41 mmol, 1 eq) was placed into a 100 mL round-bottom flask and dispersed by stirring with anhydrous pentane (50 mL) for 10 minutes. A bath with a water:methanol ratio of 3:2 (vol) was prepared, and dry ice was added to maintain a temperature of $-20\text{ }^\circ\text{C}$ in an ice bath. The mixture was stirred again for 10 minutes under these conditions. Purple solid iodine (I_2) (1.13 g, 4.46 mmol, 0.83 eq) was added, and the reaction mixture was stirred at room temperature for 12 hours. After 12 hours, the formation of opaque dispersed white material was observed, followed by filtration. Extraction was performed to remove the remaining I_2 in the filtrate. The reaction mixture was transferred to a separatory funnel, and a saturated solution of sodium thiosulfate (1M concentration, using D.I. Water) (50 mL) was added. The organic layer, a bright yellow liquid, was separated and maintained at $-78\text{ }^\circ\text{C}$. Magnesium sulfate anhydrous powder (MgSO_4) was added for moisture removal. Filtering was performed immediately as color changes occurred after storage for more than 10 minutes. After filtration, a bright yellow liquid containing pentane solvent was obtained (yield: 0.72 g, 69.3%). The product was stored in a dry ice-acetone bath at $-78\text{ }^\circ\text{C}$ for further use. ^1H NMR (C_6D_6): δ 5.04 (s, 1H), δ 5.96 (d, 2H), δ 6.10 (d, 2H).

Iodo-cyclopentadienyl tris(dimethylamino) hafnium (IHf)

In a glove box, 6.0 g (22.43 mmol, 1 eq) of white solid tetrakis(dimethylamino)hafnium was prepared in a 250 mL 3-neck round-bottom flask. Anhydrous pentane (60 mL) was added, and the mixture was stirred for 15-20 minutes in a dry ice bath at $-78\text{ }^\circ\text{C}$. While maintaining the temperature at $-78\text{ }^\circ\text{C}$, compound (2) was added dropwise over one hour using a dropping funnel. After the addition was complete, vacuum distillation was performed while maintaining $-78\text{ }^\circ\text{C}$ to remove the solvent and obtain the product (yield: 5.0 g, 54.3%). ^1H NMR (C_6D_6): δ 6.04 (t, 2H), δ 5.74 (t, 2H), δ 2.84 (s, 18H)

Computational methods

The ORCA calculation package was used for the computations²⁰. Density functional theory (DFT) calculations were performed for the geometry optimization of the molecules. Given the presence of high-atomic-number metal atoms and the potential separation of the molecule into cations and anions during molecular decomposition, the def2-TZVPPD basis set was utilized for this process. The B3LYP hybrid-type exchange-correlation energy functional was chosen. Following the structural optimization of the molecules, frequency calculations were conducted, accounting for the zero-point energy correction and the vibrational energy at a specific temperature to obtain thermodynamic properties such as enthalpy. Using this information, we determined the bond dissociation energy for the cleavage of bonds during deamination at 298 K ²¹.

Atomic layer deposition (ALD) process and metal-insulator-metal (MIM) fabrication

A substrate of 50 nm TiN was deposited as the bottom electrode by chemical vapor deposition using TiCl_4 and NH_3 . HfO_2 thin films were deposited by ALD (iOV-dX1, iSAC Research) with cyclopentadienyl

tris(dimethylamino) hafnium (CpHf) and iodo-cyclopentadienyl tris(dimethylamino) hafnium (IHf). The substrate temperature was set to 300 °C for ALD of HfO₂. O₃ was used as an oxygen source at a concentration of 170 g/m³. The canisters of CpHf and IHf were maintained at 110°C and 80°C. The ALD sequence of HfO₂ film deposition consisted of Hf precursor feeding, Ar purging, O₃ reactant feeding, and Ar purging steps of 15,20, 5, and 10 sec. After depositing the HfO₂ thin films, post-deposition annealing (PDA) was carried out at 600°C for 30 sec under a N₂ atmosphere using a rapid thermal annealing process. To fabricate MIM capacitors, a top electrode of 70 nm TiN was deposited by DC sputtering at 110°C as a dot pattern with a 300 μm diameter using a shadow mask.

Analysis of dielectric thin films

The film thickness was determined by calculating the layer density, which was measured using X-ray fluorescence spectroscopy (ARL Quant'X, ThermoFisher Scientific) and correlated with spectroscopic ellipsometry (ESM-300, J. A. Woollam) measurement and transmission electron microscopy (TEM, JEM-2100F) images. Glancing-angle-incident X-ray diffraction (GIXRD, X'pert Pro, PANalytical) at an incident angle of 0.5° was used to examine the crystal structures of the thin films. The chemical state of the dielectric thin films was investigated using X-ray photoelectron spectroscopy (XPS, K-Alpha+, ThermoFisher Scientific). The electrical properties were evaluated by measuring the capacitance versus voltage using an Agilent 4284, and the current–voltage characteristics were measured using an Agilent 4155C semiconductor parameter analyzer.

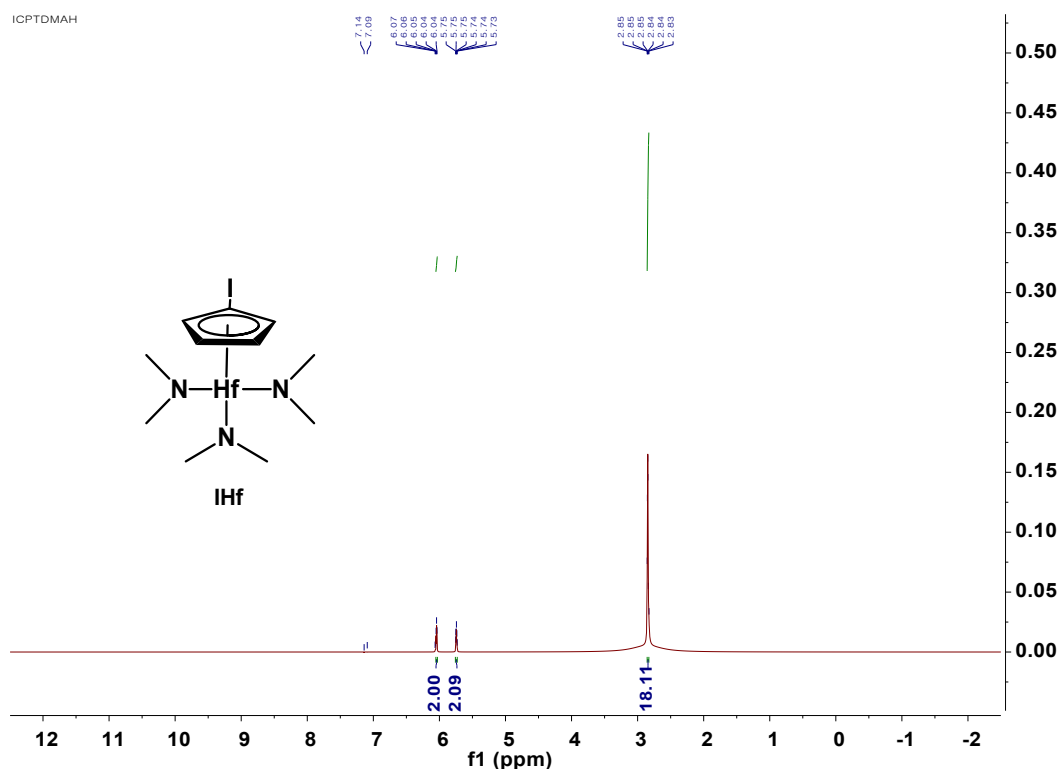


Fig. S1 ¹H NMR spectrum of IHf.

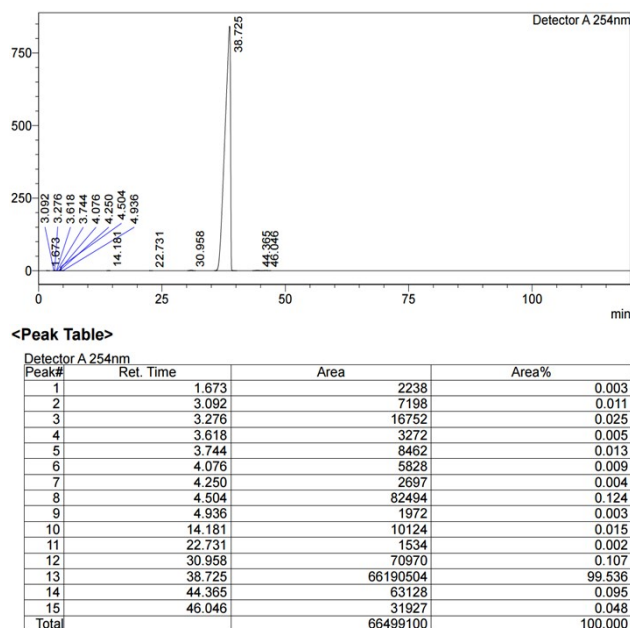


Fig. S2 High-performance liquid chromatography (HPLC) chromatograms of 5-iodocyclopentadiene (ligand compound (2)).

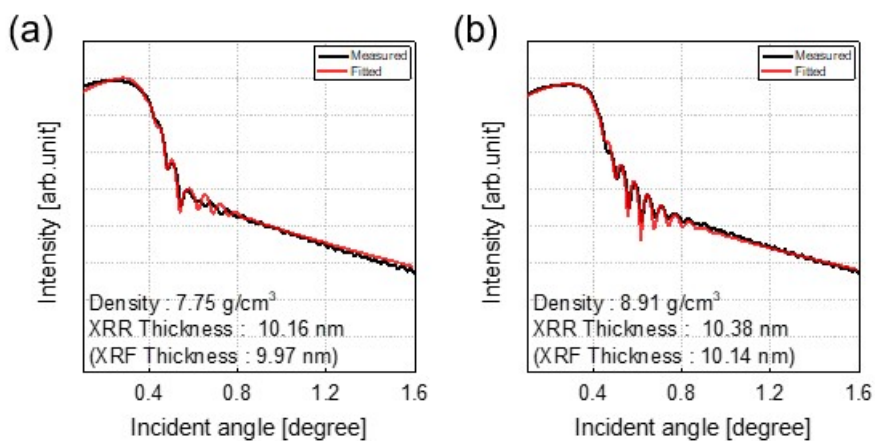


Fig. S3 XRR measurement of 10-nm-thick HfO₂ thin films deposited using (a) CpHf, and (b) IHf.

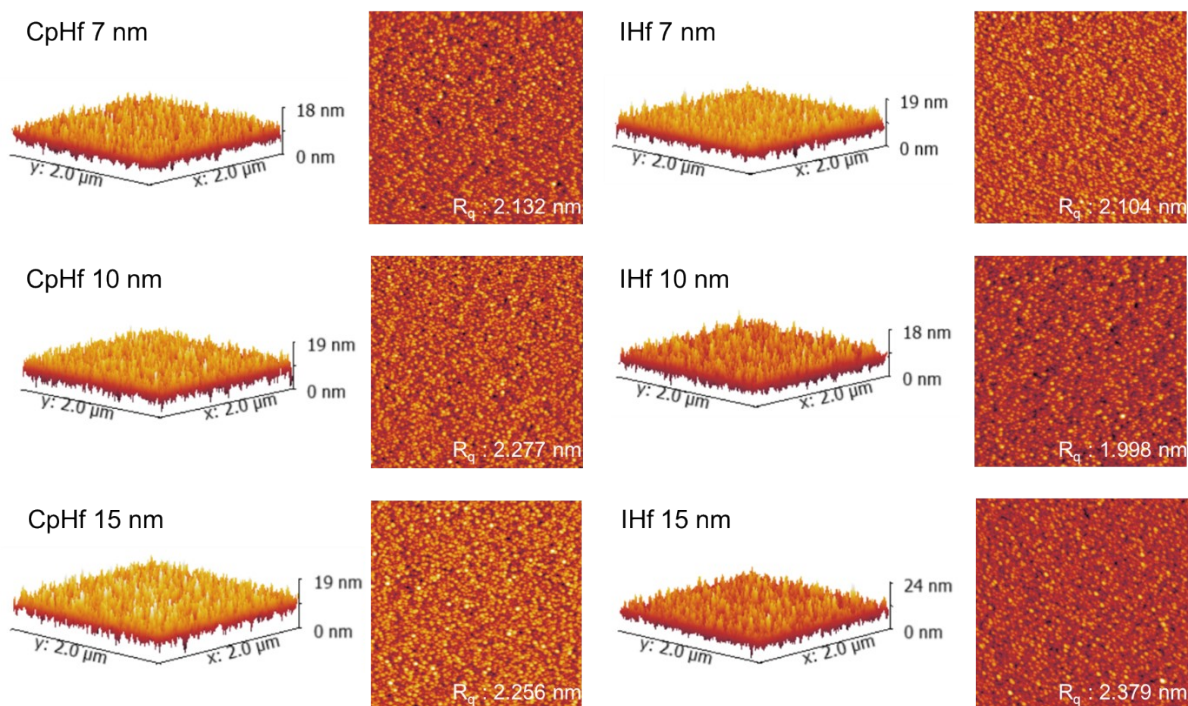


Fig. S4 AFM results of HfO_2 thin film deposited on TiN using CpHf and IHf with varied thickness.

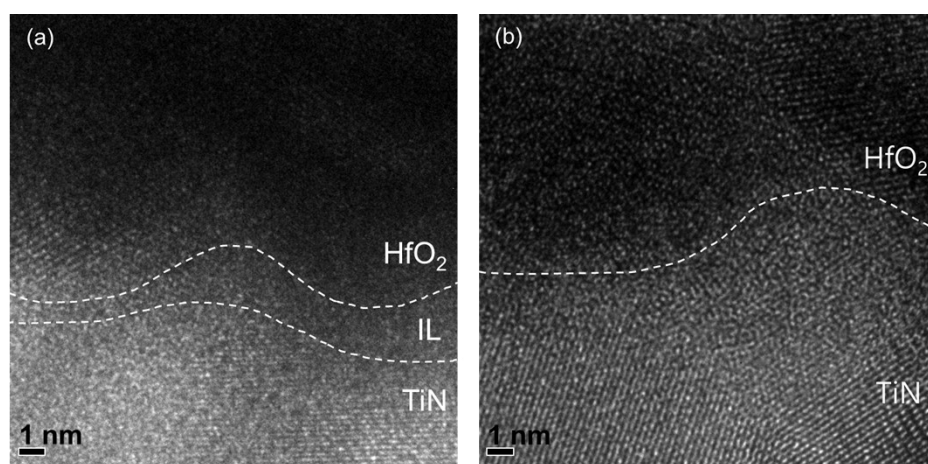


Fig. S5 TEM images of HfO_2 thin film deposited on TiN using (c) CpHf and (d) IHf.

Table S1. Bond dissociation energy.

CpHf	IHf
851.111 kJ/mol	862.117 kJ/mol

