

A Novel Liquid Hafnium Precursor for HfO Thin Film Formation

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A novel hafnium precursor, (N,N'-diisopropylacetamidinato)tris(dimethylamido)hafnium [Ts-Hf3] for chemical vapor deposition (CVD) and atomic layer deposition (ALD) was developed. This complex is liquid at room temperature and has sufficient vapor pressure and thermal stability for CVD/ALD processes. For CVD with Ts-Hf3 and O₂, HfO_x thin films were deposited on SiO₂ substrate at 140-400°C. Also, Ts-Hf3 has a wider process window than tetrakis(ethylmethylamino)hafnium(IV) [TEMAH], which led to better HfO_x thin film deposition on SiO₂ holes prepared on Si substrate with an aspect ratio of 5 at 160°C. For ALD with Ts-Hf3 and O₃, HfO_x thin films were formed on Si substrate. This compound is expected to have a wider ALD window of 250-350°C than TEMAH (240-320°C) and demonstrated better step coverage of 99% than that of 86% for CpHf(NMe₂)₃ on a L/S patterned SiO₂ substrate with an aspect ratio of 20 at 250°C. We propose Ts-Hf3 as a promising Hf precursor for CVD/ALD of HfO_x thin films.

1. INTRODUCTION

Dynamic Random Access Memory (DRAM) is a semiconductor-based memory that is widely used in personal computers, smartphones, digital home appliances, etc. As scaling of DRAM has progressed, their designs have begun to incorporate capacitors with three-dimensional structure having higher aspect ratio.¹ For the capacitors, hafnium oxide (HfO_x) is currently utilized.²

In comparison with physical vapor deposition (PVD), chemical vapor deposition (CVD) and atomic layer deposition (ALD) have been regarded as superior

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methods to achieve smooth and conformal thin films for manufacturing advanced capacitor cells. CVD/ALD precursors are generally required to have high vapor pressure and thermal stability for reliable delivery to the CVD/ALD chamber. Furthermore, these compounds are preferred to be liquid in order to heat the entire substance.

During the past some decades, various Hf complexes have been proposed as CVD/ALD precursors. Halidetype precursor, especially HfCl₄^{3,4} which is widely utilized in industry, is solid at room temperature and has low volatility. This suggests that there is difficulties in handling for CVD/ALD processes. Moreover, the use of this compound causes halogen contamination in Hf-based thin films. To improve this low volatility, amide-type precursors are employed. However, the precursors such as tetrakis(dimethylamino)hafnium(IV) [Hf(NMe₂)₄: TDMAH],⁵ tetrakis(ethylmethylamino) hafnium(IV) [Hf(NEtMe)₄: TEMAH],⁶ and Tetrakis (diethylamino)hafnium(IV) $[Hf(NEt_2)_4]^7$ are very sensitive to oxygen and/or moisture and heat-labile. These properties lead to difficulties in CVD/ALD at high temperature. Thermally stable cyclopentadienyl-type precursors⁸ like CpHf(NMe₂)₃ and (CpMe)Hf(NMe₂)₃ (Cp, cyclopentadienyl = C_5H_5) were preferred for such high temperature processes.

Herein we report the development of a novel liquid Hf complex, (N,N'-diisopropylacetamidinato) tris(dimethylamido)hafnium [Ts-Hf3], as a precursor for HfO_x thin film formation. A part of this report includes the content of the poster presentation (Program Number:14P-1-85) at 37th International Microprocesses and Nanotechnology Conference (MNC2024).⁹

Our development will contribute to reducing device power consumption through semiconductor technology innovation.

2. EXPERIMENTAL SECTION

2.1 Preparations

All manipulations were carried out under argon (Ar) atmosphere with standard Schlenk and glovebox techniques. Hexane (dehydrated grade) and TDMAH were purchased from Kanto Chemical Co. Inc. and Sigma-Aldrich Co. LLC, respectively. Benzene- d_6 (C₆D₆, obtained from FUJIFILM Wako Pure Chemical Corp.)

was purified by distillation from Na/benzophenone ketyl, and then stored under Ar. N,N'-Bis(1methylethyl)ethanimidamide ['PrN(H)C(Me)=N'Pr] was prepared according to a literature procedure.¹⁰ TEMAH was obtained from Sigma-Aldrich Co. LLC and used for a deposition test without further purification. ¹H-NMR spectra were recorded on a Bruker Avance HD 400 MHz spectrometer at 293 K.

Synthesis of Ts-Hf3

^{*i*}PrN(H)C(Me)=N^{*i*}Pr (1.81 g, 12.7 mmol) was slowly added to a solution of TDMAH (4.48 g, 12.6 mmol) in hexane (20 mL) at -20° C. The reaction mixture was warmed to room temperature and then stirred for 12 h. After the removal of solvent under reduced pressure, the residue was purified by distillation under reduced pressure (80°C, 15 Pa) to give Ts-Hf3 as a colorless to pale yellow liquid (4.00 g, 70%). ¹H-NMR (400 MHz, C₆D₆, δ /ppm): 3.45 (sept, *J* = 7 Hz, 2H), 3.15 (s, 18H), 1.49 (s, 3H), 1.05 (d, *J* = 7 Hz, 12H). ¹³C-NMR (100 MHz, C₆D₆, δ /ppm): 175.9, 48.1, 42.8, 25.2, 11.1.

2.2 Measurement of Physical Properties

Thermogravimetric analysis (TG) was carried out under an Ar flow (400 mL/min) at a heating rate of 10°C/min with a SII Technology TG/DTA7200 that was contained in a nitrogen-filled glovebox to prevent decomposition arising from exposure to air. Differential scanning calorimetry analysis (DSC) was performed using a SII Technology DSC7020 at a heating rate of 10 °C/min with a sealed container in an Ar gas atmosphere. The sample weights used for TG and DSC were 19.2 and 5.0 mg, respectively. Vapor pressures were estimated by a diaphragm gauge (Baratron[®]) placed in a thermostatic oven.

2.3 Deposition of HfO_x Thin Films

HfO_x thin film deposition was conducted by CVD and ALD methods. The deposition apparatus was illustrated in **Fig.1** and **2** and the typical deposition conditions were shown in **Table 1**. The Hf precursors were selected from Ts-Hf3, TEMAH and CpHf(NMe₂)₃. These Hf compounds were vaporized by a bubbling method with the vapor pressures of 0.13 Torr at 80°C (Ts-Hf3), 60°C (TEMAH), and 60°C [CpHf(NMe₂)₃]. These vapors were transferred to CVD or ALD reactor chamber using

Ar carrier gas. Ar is also used for a diluent gas.







Fig. 2 ALD apparatus

Table 1	Typical Deposition Conditions
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Deposition method	CVD	ALD			
Hf precursors	Ts-Hf3 or TEMAH	Ts-Hf3 or CpHf(NMe ₂) ₃			
Co-reactant	O2 (120 sccm)	O ₃ (30 or 10 sccm)			
Carrier gas	Ar (30 sccm)	Ar (10 sccm)			
Diluent gas	Ar (250 sccm)	Ar(70 sccm)			
Depo. temp.	140-400 °C	250-400°C			
Depo. press.	4 Torr	0.8 or 2.3 Torr			
Depo. time	60 min	-			
		Hf→Vac→Purge→			
ALD sequence	-	O ₃ →Vac→Purge			
Substrate	SiO ₂ (100 nm)/Si	Si or L/S patterned SiO ₂			

2.4 Evaluation of HfO_x Thin Films

Film thickness was estimated by the X-ray fluorescence (XRF) calibrated by standard samples. The crystallinity and the atomic composition of the films were analyzed by means of X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) after Ar⁺ sputtering, respectively. Transmission electron microscopy (TEM) was used to evaluate conformality of the deposited films.

3. RESULTS AND DISCUSSION

3.1 Molecular Design, Synthesis, Physical and Chemical Properties of Ts-Hf3

As an excellent CVD/ALD precursor having high thermal stability and low melting point, the novel hafnium complex [Ts-Hf3] was designed with an asymmetrical structure and amidinate ligand. Ts-Hf3 can be synthesized by treatment of TDMAH with ^{*i*}PrN(H)C(Me)=N^{*i*}Pr, followed by purification by vacuum distillation (**Fig. 3**).

The basic properties of Ts-Hf3 are summarized in Table 2. The Hf complex is a liquid at room temperature. The volatility and the thermal decomposition temperature of this compound were analyzed by TG and DSC, respectively (Fig. 4 and 5). Ts-Hf3 exhibited single-step weight loss with almost no residue on the TG curve. In DSC, the exothermic peak due to pyrolysis started around 260°C. Comparing the peak temperatures of Hf complexes, Ts-Hf3 shows higher thermal stability than TEMAH, which implies the amidinate ligand in Ts-Hf3 enhances its stability. Also, the Clausius-Clapeyron plots of Ts-Hf3 are presented in Fig. 6, and the vapor pressures were determined to be 0.1 Torr at 77℃ and 1.0 Torr at 118℃. The vapor pressure is significantly higher than that of HfCl₄ (1.0 Torr at 170°C),⁴ and almost equivalent to the amide-type liquid Hf precursors like TEMAH (1.0 Torr at 113°C) and Hf(NEt₂)₄ (1.0 Torr at 126° C).⁷

These results indicate that Ts-Hf3 has sufficient volatility and favorable thermal stability for use as a precursor for the CVD/ALD processes.



Fig. 3 Synthetic route of Ts-Hf3

Structure				
Appearance	Colorless to pale yellw liquid			
Melting point	<-20°C			
Vapor pressure	0.1 Torr @ 77℃ 1.0 Torr @118℃			
Thermal decomp. temp.	260℃ or higher			

Table 2 Basic Properties of Ts-Hf3



Fig. 4 TG curve of Ts-Hf3



Fig. 5 DSC curves of Ts-Hf3 (red) and TEMAH (blue)



Fig. 6 Clausius-Clapeyron plots of Ts-Hf3

3.2 CVD with O₂

The Arrhenius plots of the deposition rates versus 1000/T are shown in Fig. 7 at $140-400^{\circ}C$ on SiO₂ substrate under 4 Torr of deposition pressure from Hf precursors (Ts-Hf3 and TEMAH) and O₂. The deposition rates of HfO_x thin films formed by Ts-Hf3 and TEMAH were constant regardless of the deposition temperature above 270°C and 200°C, respectively. This result indicates that CVD in this temperature region is dominated by mass-transport-limited process. On the other hand, the deposition rates were decreased below 270°C (Ts-Hf3) and 200°C (TEMAH). This phenomenon represents that the deposition rate is controlled by a reaction-limited process, and Ts-Hf3 has a wider process window than that of TEMAH.



Fig. 7 Temperature dependency of deposition rate of HO_x thin films formed by CVD of Ts-Hf3 or TEMAH with O_2 on SiO_2 substrate

The step coverage of HfO_x thin film from Ts-Hf3 was investigated by using hole patterned substrate and compared with that from TEMAH. These films were deposited on SiO₂ holes prepared on Si substrate with an aspect ratio of 5 at 160°C. The detailed deposition conditions are shown in **Table 3**. Cross-sectional TEM images of the films are presented in **Fig. 8**. For Ts-Hf3, it was confirmed that the film was formed over the entire surface of the hole. However, almost no HfO_x thin film from TEMAH was deposited on the bottom region. These results reflect the fact that Ts-Hf3 has the wider process window with O₂ than TEMAH, and this suggests that the amidinate ligand in Ts-Hf3 increases the stability of the complex, allowing it to be transported to the bottom of the hole without decomposition.

Hf precursors	Ts-Hf3 or TEMAH				
Co-reactant	O2 (60 sccm)				
Carrier gas	N2 (20 sccm)				
Diluent gas	N2 (220 sccm)				
Depo. temp.	160 °C				
Depo. press.	4 Torr				
Depo. time	60 min				
Substrate	SiO ₂ /Si				
Hole diameter	150 nm				
Aspect ratio	5				

 Table 3
 CVD Conditions of HfOx Thin Films on Hole Patterned Substrate



Fig. 8 Cross-sectional TEM images of HfO_x thin films by CVD of Ts-Hf3 (left) or TEMAH (right) with O₂ on SiO₂ holes prepared on Si substrate at 160°C

3.3 Characterization of HfO_x Thin Films Formed by CVD with Ts-Hf3 and O₂

Fig. 9 represents XRD patterns of HfO_x thin films formed from Ts-Hf3 and O_2 on SiO₂ substrate at 400, 350, 300, and 270°C. Below 350°C, almost no crystalline peaks were detected, indicating that these HfO_x thin films are amorphous. At a high temperature of 400°C, HfO_2 crystalline thin film was demonstrated without annealing treatment.

3.4 ALD with O₃

Before performing the detailed HfO_x -ALD with Ts-Hf3 and O_3 , the optimal ALD parameters were investigated (**Fig. 10**a, b). The feed time of Ts-Hf3 and the vacuum + purge time were saturated at 2 seconds or more and at least 5 seconds or more, respectively. **Fig. 10**c shows film thickness of HfO_x thin films versus ALD cycle number by employing Ts-Hf3 and O_3 (30 sccm) on Si substrate at 250°C under 2.3 Torr of deposition pressure. The film thickness was increased with



Fig. 9 XRD patterns of HfOx thin films from Ts-Hf3 and O2 on SiO2 substrate at 400, 350, 300, and 270°C

increasing number of cycles and the incubation cycle appeared to be negligible.

Next, ALD of HfO_x thin film employing Ts-Hf3 and O_3 (30 sccm) was carried out on Si substrate at 250, 300, 350, and 400°C under 2.3 Torr (**Fig. 10**d). The ALD sequence was Ts-Hf3 (2.0 s), vacuum (4.0 s), Ar purge (6.0 s), O_3 (3.0 s), vacuum (2.0 s), and Ar purge (3.0 s) for 100 cycles. The growth per cycle (GPC) was nearly constant in the temperature range from 250 to 350°C, which suggests a wide ALD window for Ts-Hf3. On the other hand, the reported ALD window for TEMAH and



Fig.10 Growth per cycle of HfOx thin films as a function of (a) Ts-Hf3 feed time and (b) vacuum + purge time after Ts-Hf3 feed by using Ts-Hf3 and O₃ (30 sccm) on Si substrate at 250°C under 2.3 Torr. (c) Film thickness of HfOx thin films as a function of ALD cycle number by employing Ts-Hf3 and O₃ (30 sccm) on Si substrate at 250°C under 2.3 Torr. (d) Growth per cycle of HfOx thin films by using Ts-Hf3 and O₃ (30 sccm) on Si substrate at 250, 300, 350, and 400°C under 2.3 Torr.

 O_3 is 240-320°C.¹¹ This implies that Ts-Hf3 has broader process applicability than TEMAH. It is also known that CpHf(NMe₂)₃ and O₃ show almost the same ALD window of 250-350°C as that of Ts-Hf3, but the GPC of about 0.75 Å/cycle is lower than that of Ts-Hf3.⁸

The step coverage of HfO_x thin film from Ts-Hf3 and O_3 was examined comparing with CpHf(NMe₂)₃. The ALD sequence was Hf precursor (10.0 s), vacuum (6.0 s), Ar purge (5.0 s), O_3 (3.0 s), vacuum (3.0 s), and Ar purge (5.0 s) for 120 (Ts-Hf3) or 130 [CpHf(NMe₂)₃] cycles. These films were formed using O_3 (10 sccm) on a L/S patterned SiO₂ substrate with an aspect ratio of 20 and a critical dimension of 50 nm at 250°C under 0.8 Torr. Cross-sectional TEM images of the thin film for Ts-Hf3 demonstrated excellent step coverage of 99%, whereas the coverage for CpHf(NMe₂)₃ was 86% (Fig. 11).

3.5 Characterization of HfO_x Thin Films Formed by ALD with Ts-Hf3 and O_3

XPS was performed to investigate the chemical composition of the deposited films by ALD of Ts-Hf3 and O_3 (30 sccm) on Si substrate at 250, 350, and 400°C under 2.3 Torr (**Table 4**). The thin film formed at 250°C contained a trace amount of carbon, while no impurities of C, N, or Si were found in the films obtained at 350°C and 400°C. This shows that Ts-Hf3 can form a thin film consisting mostly of Hf and O.



Fig.11 Cross-sectional TEM images of HfOx thin films formed by ALD of Ts-Hf3 (left) or CpHf(NMe2)3 (right) with O3 (10 sccm) on a L/S patterned SiO2 substrate with an aspect ratio of 20 and acritical dimension of 50 nm at 250°C under 0.8 Torr

Table 4	Chemical Composition of HfOx Thin Films Deposited
	with Ts-Hf3 and O ₃ (30 sccm) on Si Substrate at 250,
	350, and 400°C under 2.3 Torr

Substrate	Substrate	Film	Chemical composition				
temperature		tnickness	[atom%]				
[°C]		[nm]	Hf	С	Ν	0	Si
250	Si	28	53	1	ND	46	ND
350	Si	35	53	ND	ND	47	ND
400	Si	24	55	ND	ND	45	ND

4. SUMMARY AND CONCLUSIONS

A molecular design and a synthetic procedure along with physical and chemical properties were presented for a new Hf precursor, Ts-Hf3. This complex is liquid at room temperature and has sufficient vapor pressure and favorable thermal stability for CVD/ALD processes.

For CVD with Ts-Hf3 and O_2 , Hf O_x thin films were deposited on Si O_2 substrate at 140-400°C. Ts-Hf3 has a wider process window than TEMAH, which led to better Hf O_x thin film deposition on Si O_2 holes prepared on Si substrate with an aspect ratio of 5 at 160°C.

For ALD with Ts-Hf3 and O_3 , HfO_x thin films were formed on Si substrate. This compound is expected to have a wider ALD window of 250-350°C than TEMAH (240-320°C) and higher GPC of ~1.0 Å/cycle than that of ~0.75 Å/cycle for CpHf(NMe₂)₃ at 250-350°C. Additionally, Ts-Hf3 demonstrated better step coverage of 99% than that of 86% for CpHf(NMe₂)₃ on a L/S patterned SiO₂ substrate with an aspect ratio of 20 at 250°C.

Thus, Ts-Hf3 is a promising CVD/ALD precursor for HfO_x thin film formation.

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6. REFERENCES

- (1) M. Jung, V. Gaddam, and S. Jeon, *Nano Converg*.9, 44 (2022)
- (2) H. Choi, Y. H. Cho, S. H. Kim, K. Yang, and M. H.
 Park, *J. Phys. Chem. Lett.*, **15**, 983 (2024)

- (3) A. B. Mukhopadhyay, C. B. Musgrave, and J. F. Sanz, *J. Am. Chem. Soc.*, 130, 11996 (2008)
- (4) A. A. Palko, A. D. Ryon, and D. W. Kuhn, *J. Phys. Chem.*, **62**, 319 (1958)
- (5) K. Kukli, T. Pilvi, M. Ritala, T. Sajavaara, J. Lu, and M. Leskelä, *Thin Solid Films*, **491**, 328 (2005)
- (6) K. Kukli, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskelä, *Chem. Vap. Deposition*, 8, 199 (2002)
- (7) D. M. Hausmann, E. Kim, J. Becker, and R. G. Gordon, *Chem. Mater.*, 14, 4350 (2002)
- (8) J. Niinistö, M. Mäntymäki, K. Kukli, L. Costelle, E. Puukilainen, M. Ritala, and M. Leskelä, *J. Cryst. Growth*, **312**, 245 (2010)
- (9) S. Ikemura, Y. Yamamoto, R. Ebihara, H. Oike, K. Tokudome, K. Iwanaga, and K. Tada: A Novel Liquid Hafnium Precursor for Conformal HfO ALD. Poster presented at: 37th International Microprocesses and Nanotechnology Conference (MNC2024); November 14, 2024; Kyoto, Japan.
- (10) A. C. Lamb, Z. Wang, T. M. Cook, B. Sharma, S.-J. Chen, Z. Lu, C. A. Steren, Z. Lin, and Z.-L. Xue, *Polyhedron*, **103**, 2 (2016)
- (11) S. Y. Lee, H. K. Kim, J. H. Lee, II.-H. Yu, J.-H. Lee, and C. S. Hwang, *J. Mater. Chem. C*, 2, 2558 (2014)