Review of Atomic Layer Deposition of Hafnium Alkylamides and Different Oxygen Precursors 3.1.2026

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Saku Turkkulainen – ID 716404
Supervised by: Ville Miikkulainen

1 Introduction

As the dimensions of transistors continue to shrink, research in high-k dielectric materials is needed. Commonly studied and industrially adopted high-k oxides include TiO_2, ZrO_2, and HfO_2. From these, hafnium dioxide has become widely used dielectric material in integrated circuits, and was first used in commercial integrated circuits by Intel in 2007. Modern integrated circuits use complex three-dimensional architectures which require highly conformal and uniform thin films.

Atomic layer deposition (ALD) is an established thin film deposition technique that enables precise thickness control from a few atomic layers to several hundred nanometers. ALD is based on self-limiting surface reactions, which result in conformal and uniform films. In addition, ALD can operate at lower temperatures than chemical vapor deposition (CVD), making it fit for temperature-sensitive processes and substrates.

Metal alkylamides are commonly used as ALD precursors because they do not introduce halogen impurities into the film. Their reaction byproducts are less corrosive than those of halide-based precursors, which reduces film etching and improves process safety. Hafnium alkylamides are reactive and sufficiently volatile compounds that have been widely used with various oxygen sources. These include H_2O, O_3, O_2 plasma, and H_2O_2 [1–11].

In this work, we review existing literature on the effects of alkylamide ligand structure and oxygen precursor selection on growth per cycle (GPC), film conformality, surface roughness, and film composition. The focus is on hafnium alkylamides tetradimethylamidohafnium (TDMAH), tetraethylmethylamidohafnium (TEMAH), and tetradiethylamidohafnium (TDEAH).

2 Results

2.1 Alkylamides as precursors

Hafnium alkylamides are metalorganic compounds with a central hafnium atom bonded to alkylamide ligands. These ligands can be homoleptic or heteroleptic, depending on whether the ligands are identical or not, respectively. Common homoleptic hafnium alkylamides include TDMAH, TEMAH and TDEAH. The molecular structures of these compounds are shown in Figure 1.

As the hydrocarbon ligand chains become longer, the volatility of the precursor decreases. This means that higher source temperatures are required to achieve sufficient vapor pressure. Also, longer ligands generally increase thermal stability and raise the decomposition temperature. This trend is shown in Figure 2.

A commonly proposed reaction mechanism for alkylamide and water-based ALD processes is shown in Figure 3. More detailed density functional theory (DFT) studies have been reported for the TEMAH + H_2O process [12] and the TDMAH + H_2O process [13]. A mechanistic investigation of the TDMAH and elemental oxygen process

has also been reported [14].

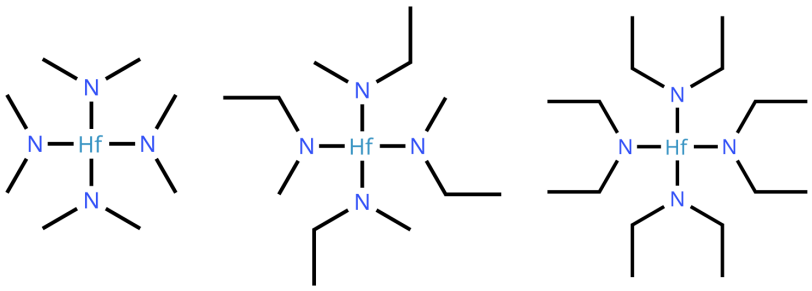

Figure 1: From left to right: TDMAH, TEMAH, and TDEAH. Structures were drawn with moldraw.com.

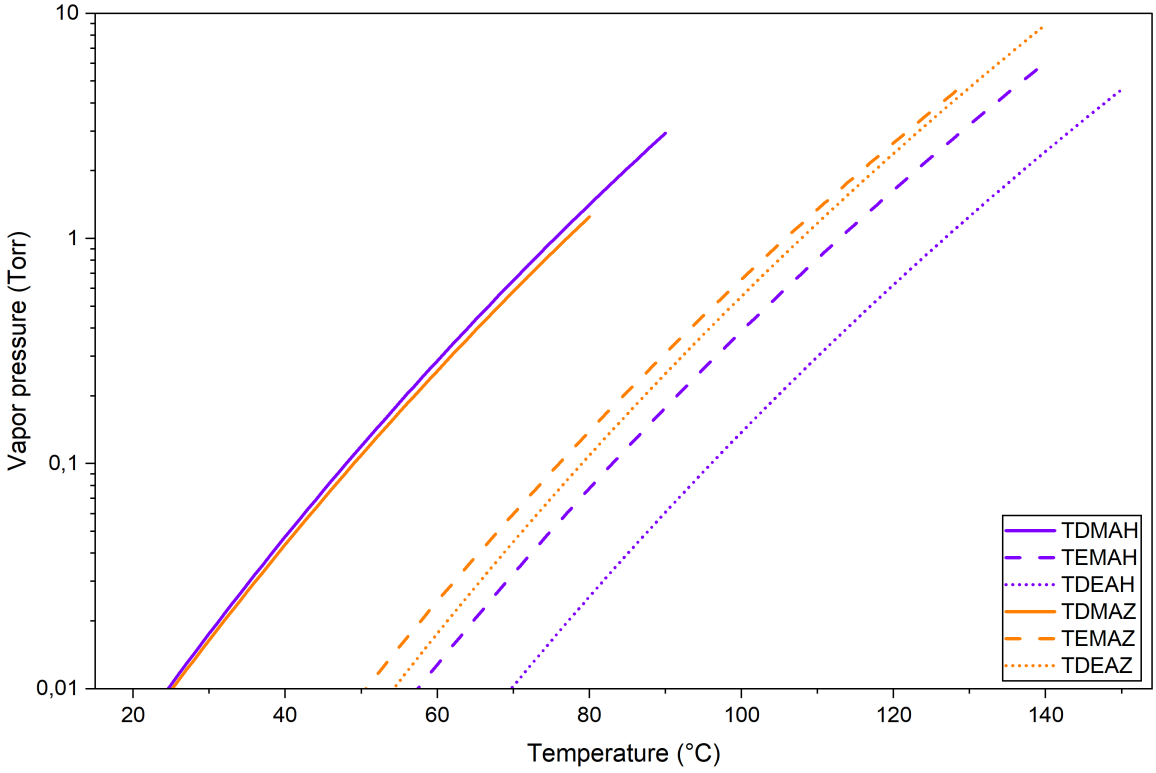

Figure 2: Vapor pressures of TDMAH, TEMAH, TDEAH, tetradimethylamidozirconium (TDMAZ), tetraethylmethylamidozirconium (TEMAZ), and tetradiethylzirconium (TDEAZ) as a function of temperature calculated with the Clausius-Clapeyron equation from 0.01 Torr until decomposition. Data from[1].

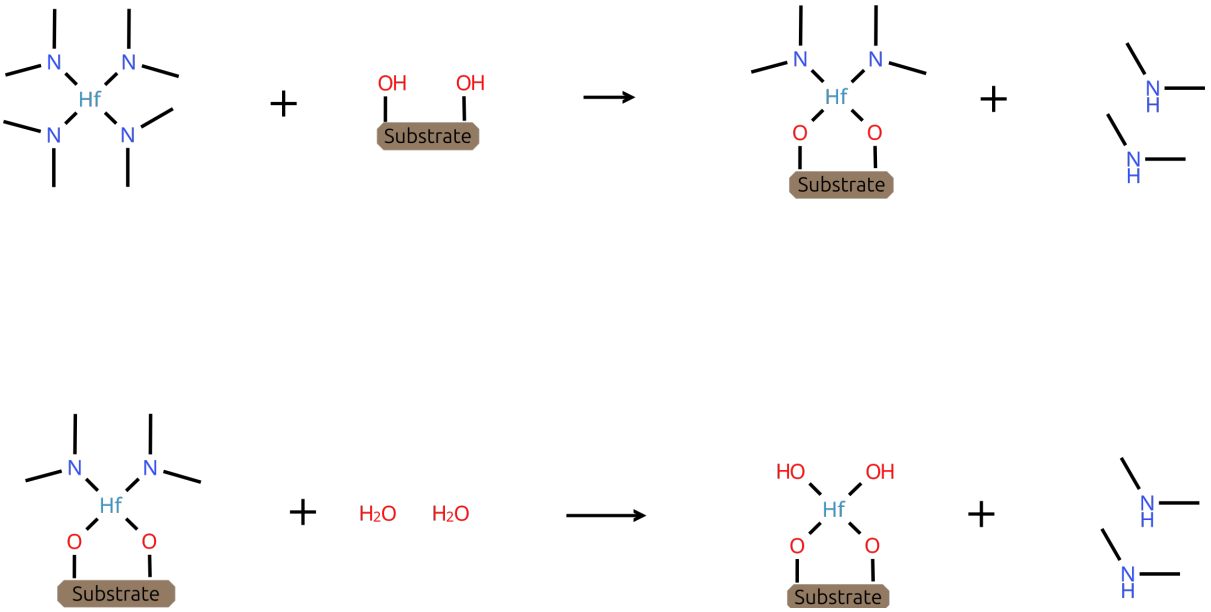

Figure 3: Commonly proposed reaction mechanism for alkylamides and water. Figure was inspired by[1].

2.2 Growth per Cycle and Density

The growth per cycle (GPC) of HfO_2 films depends strongly on both the metal precursor and the oxygen source. Provine et al. deposited HfO_2 films using TDMAH with O_2, O_2 plasma, and H_2O [2]. The highest GPC values, approximately 1.0–1.1 Å per cycle, were obtained using H_2O and O_2 plasma. In contrast, molecular O_2 produced low GPC values of 0.1–0.2 Å per cycle. The O_2 process did not show self-limiting behavior even for long pulse times, which suggests kinetically limited oxidation. Although increasing the O_2 exposure improved film density, these films remained less dense than those deposited using plasma or water.

Processes using molecular oxygen are highly sensitive to trace moisture. Bhatia et al. demonstrated that even small amounts of water vapor can significantly increase the GPC of TiO_2 films deposited using O_2 [15]. Similar effects are expected for HfO_2 processes.

For TEMAH-based processes, Kukli et al. reported GPC values between 0.56 Å and 0.75 Å when using water in the temperature range of 205–300 °C [3]. The resulting films exhibited relatively high density and low surface roughness. It is noteworthy that the film thicknesses were less than 5 nm. Senzaki et al. reported that when ozone was used instead of water, higher GPC values of approximately 0.86 Å were achieved at 250–300 °C [7]. This increase is consistent with the stronger oxidation potential of ozone.

TDEAH generally yields higher GPC values than TDMAH and TEMAH. Deshpande et al. reported a GPC of 1.4 Å at 300 °C using H_2O as the oxidant [4]. Plasma-assisted processes produced similar values. Kim et al. compared remote plasma ALD and direct plasma ALD using TDEAH and O_2 plasma at 250 °C [9]. GPC values of 1.0 Å and 1.1 Å were reported, respectively. Remote plasma ALD produced films with better electrical properties. Katamreddy et al. also reported GPC values near 1.1 Å for

TDEAH and O_3 between 200 °C and 275 °C [8].

Overall, the GPC of hafnium alkylamide precursors increases with ligand size and follows the trend: TDEAH > TEMAH > TDMAH.

These results highlight the combined influence of precursor chemistry and oxidant strength on growth rate and film density.

Table 1: GPC values of HfO_2 films grown with different precursors.

Hf precursor	O precursor	Temperature (°C)	GPC	Ref.
TDMAH	O_2	200–370	0.3–0.9	[6]
TDMAH	O_2	150–250	0.0–0.5	[2]
TDMAH	O_3	200	0.9–1.0	[6]
TDMAH	O_2 plasma	200	1.0–1.1	[2]
TDMAH	H_2O	200	1.1	[2]
TEMAH	O_2	200	0.4	[16]
TEMAH	O_3	250–300	0.86	[7]
TEMAH	O_2 plasma	250	1.1	[17]
TEMAH	O_2 plasma	100–250	1.3–1.4	[10]
TEMAH	H_2O	205–300	0.56–0.75	[3]
TDEAH	O_3	200–275	1.1	[8]
TDEAH	O_2 plasma	250	1.0–1.1	[9]
TDEAH	H_2O	300	1.4	[4]

2.3 Roughness and Conformity

Surface roughness is important for HfO_2 films, especially in gate dielectric and high-aspect-ratio applications. Roughness affects interface quality, leakage current, and device reliability. The roughness of ALD-grown HfO_2 films depends on deposition temperature, oxidant chemistry, and growth regime.

High conformality has been reported for TDMAH and ozone processes. Liu et al. demonstrated uniform step coverage on structures with aspect ratios up to 35 [6]. Similar conclusions were reported for TiO_2 deposition using titanium–TDMA precursors and molecular oxygen [2]. These results suggest that elemental oxygen can support conformal growth under appropriate conditions. Gieraltowska et al. reported a strong temperature dependence of surface roughness for TDMAH and water processes [18]. 500 nm films deposited at 85 °C were amorphous and had RMS roughness of 1 nm. Films deposited at 100 °C were polycrystalline and had higher RMS roughness of 21 nm. Roughness decreased with increasing temperature and reached a minimum of 4 nm at 350 °C. This trend was due to improved surface reactions and increased film density.

Hausmann and Gordon studied HfO_2 films deposited from TEMAH and water using atomic force microscopy[19]. They observed that RMS roughness increased with deposition temperature. Films grown at 50 °C had RMS roughness of 1 %, while films deposited between 150 °C and 250 °C showed RMS roughness of up to 5 %. This increase was due to enhanced surface diffusion and the onset of crystallization at higher

temperatures. Liu et al. studied the effect of oxidant choice by depositing HfO_2 using TEMAH with ozone, water, and oxygen [16]. Although conformal films were obtained on planar substrates, high-aspect-ratio structures showed non-uniform thickness at elevated temperatures. This was due to ozone decomposition before complete surface saturation in deep structures. Kukli et al. reported low roughness values between 0.4 nm and 0.8 nm for TEMAH and water processes using X-ray reflectivity [3]. These results demonstrate that smooth and dense HfO_2 films can be achieved under optimized ALD conditions.

2.4 Film Composition

An interfacial layer containing silicon and oxygen is commonly formed between silicon substrates and HfO_2 films. Kim et al. proposed that ligand desorption and incomplete oxidation contribute to interfacial layer growth [20].

Ko et al. studied HfO_2 films deposited using TDMAH with water, ozone, and mixed ozone–water sequences [21]. Films deposited using a combination of ozone and water crystallized without annealing due to increased oxygen content. Water-based processes produced higher carbon and nitrogen impurity levels than ozone-based processes. This difference was attributed to the stronger oxidation potential of ozone. Gieraltowska et al. reported that TDMAH and water processes resulted in films containing approximately 6 % carbon and 4.5 % nitrogen over a wide temperature range [18]. Thicker interfacial layers were also observed when deposition temperature was over 100 °C. While, Ko et al. reported impurity levels below 1 % for ozone-based and ozone + water processes.

Liu et al. studied TEMAH-based processes using water and ozone [16]. Film purity improved with increasing temperature. Water-based films maintained carbon and hydrogen impurity levels at or below 1 % from 200 °C to 320 °C. Ozone-based films showed higher impurity levels at lower temperatures but reached similar purity at 320 °C. Senzaki et al. reported nitrogen impurity levels below 1 % and carbon concentrations of 2–4 % for TEMAH and ozone processes [7]. Kukli et al. reported that hydrogen impurities can be reduced through post-deposition annealing [22].

Table 2: Compositions of HfO_2 films grown with different precursors.

Hf source	O source	Temp. (°C)	O/Hf	C-%	H-%	N-%	Ref.
TDMAH	O_3	250	2.00	4.3	3.0	0.4	[7]
TDMAH	O_3	300	1.97	2.5	2.8	0.8	[7]
TDMAH	H_2O	100	2.03	6.0	-	4.5	[18]
TDMAH	H_2O	200	1.94	6.0	-	4.5	[18]
TEMAH	O_3	200	-	10.0	5.5	-	[16]
TEMAH	O_3	250	-	5.8	2.3	-	[16]
TEMAH	O_3	320	2.04	0.8	0.5	-	[16]
TEMAH	H_2O	200	-	1.0	0.7	-	[16]
TEMAH	H_2O	250	-	0.5	0.5	-	[16]
TEMAH	H_2O	320	2.04	0.5	0.5	-	[16]

3 Conclusions

This review summarizes literature on ALD of HfO_2 using hafnium alkylamide precursors and various oxygen sources. Direct comparison of reported results is challenging due to differences in substrates, reactor designs, and post-deposition treatments. Film properties are sensitive to surface preparation, deposition parameters, and annealing conditions. In addition, some interesting material properties depend strongly on measurement techniques and instrument settings. These include electrical properties such as the dielectric constant and leakage current. Despite these limitations, trends can be identified regarding precursor reactivity, oxidant strength, and their impact on growth behavior, roughness, and film composition. Molecular oxygen tends to be less reactive than water or ozone. The films have lower densities and the process times are longer.

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