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Atomic Layer Deposition of HfO_2 Thin Films Exploiting Novel Cyclopentadienyl Precursors at High Temperatures

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Atomic layer deposition (ALD) of HfO_2 thin films was studied using four novel cyclopentadienyl precursors, namely, $(CpMe)_2HfMe_2$, $Cp_2Hf(OMe)_2$, $(CpMe)_2Hf(OMe)Me$, and $(CpMe)_2Hf(OMe)_2$. Ozone was used as the oxygen source. Among the cyclopentadienyl precursors, $(CpMe)_2HfMe_2$ and $(CpMe)_2Hf(OMe)Me$ were the most promising, showing ALD-type growth characteristics at high temperatures as the self-limiting growth mode was confirmed at 400 °C. ALD-type growth was verified also on 60:1 aspect ratio trench structures even at 450 °C, where perfect conformality was obtained. The growth rate stayed nearly constant at around 0.5 Å/cycle at substrate temperatures between 350 and 500 °C. When $Cp_2Hf(OMe)_2$ and $(CpMe)_2Hf(OMe)_2$ were applied, slight decomposition of the precursor was detected at 350−400 °C, and thus a self-limiting growth mode was not achieved. Time-of-flight elastic recoil detection analyses demonstrated stoichiometric HfO_2 films, where impurity concentrations were below 0.1 at % for C, H, and N in films deposited from each of the four Hf precursors. In addition, thin HfO_2 films showed good dielectric properties such as low hysteresis, nearly ideal flatband voltage, and effective permittivity values similar to previously reported HfO_2 films obtained by the alkylamide-based processes.

Introduction

In microelectronics, the continuous shrinking of device size is necessary to improve the performance, which sets challenging requirements for the integrated circuit fabrication. New materials and techniques are required and materials must be grown in the form of very thin films into deep trenches and other 3D structures with good conformality. As requirements tighten, novel thin film deposition techniques are needed in many applications. Atomic layer deposition (ALD) technology, originally known as atomic layer epitaxy, has particularly gained interest in the microelectronics industry because of the unique characteristics that this method offers: ultrathin films can be deposited on a large substrate area with excellent conformality and a control of thickness and composition at the nanometer level.[1,2] ALD is an advanced variant of the chemical vapor deposition (CVD) method, but unlike CVD, ALD relies on sequential and saturating surface reactions of the alternately applied precursor pulses. The precursor pulses are separated by inert gas purging or evacuation of the reaction chamber to avoid gas-phase reactions between the precursors. The growth proceeds in a cyclic manner, enabling facile thickness control. ALD has high potential in microelectronics for the growth of high permittivity (high-*k*) films to replace SiO_2-based solutions as insulators for complementary metal oxide semiconductor devices and dynamic random access memory (DRAM) capacitors. Other microelectronic applications of ALD-grown materials include ferroelectrics, barrier materials, and conductors such as metal gates.[2−4] In DRAM trench capacitor structures, the capacitors are constructed into high-aspect-ratio trenches in order to increase the surface area and thus the effective capacitance density. A near-future solution for high-*k* materials in trench capacitor structures is similar, as in the case of gate dielectric applications where Hf-based materials have been applied. As the trench aspect ratio is expected to increase up to 80:1 by the year 2007, ALD is considered as the only viable technique for such depositions.[5]

As ALD is a chemical deposition method, the precursor chemistry has a decisive effect on the quality and properties of the deposited films.[6,7] The most commonly used Hf precursor, $HfCl_4$, has potential drawbacks such as chlorine contamination of the films[8] and the generation of particles and corrosive byproducts during the ALD processing.[7] The use of volatile and liquid hafnium alkylamides, especially

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Table 1. ALD Related Properties of Hafnium Cyclopentadienyl Precursors

precursor	solid/liquid at 20 °C	melting point (°C)	sublimation/ evaporation T at 2−3 mbar (°C)	vapor pressure @ P = mmHg, T = K
$(CpMe)_2HfMe_2$	solid	∼60	60 (liquid)	$\log P = 8.4162 - 3223.9/T$
$Cp_2Hf(OMe)_2$	solid	70−72	60 (partly solid)	$\log P = 15.206 - 5058.6/T$
$(CpMe)_2Hf(OMe)Me$	liquid	n/a	62 (liquid)	$\log P = 6.4697 - 2555.9/T$
$(CpMe)_2Hf(OMe)_2$	solid	∼30	65 (liquid)	n/a

$Hf(NEtMe)_4$, with water can provide excellent thickness uniformity and conformality[9] but also yield films with considerable impurity content; e.g., 0.3−0.6 at % C and 2−3 at % H when the $Hf(NEtMe)_4/H_2O$ ALD process is applied at 250 °C.[10] The suitable ALD growth temperature range for the Hf alkylamide processes to obtain excellent film properties is rather limited, as the growth temperatures exceeding 300 °C decompose the alkylamide precursor, prevent the ALD-type growth mode, and result in poor film uniformity.[10,11] The thermal stability is limited for the Hf-alkoxides as well.[12] Higher processing temperatures would be beneficial for industrial production, as higher growth temperatures are known to produce dense films with less impurities and defects.[6] In addition, a wider ALD temperature window allows more possibilities when combining with other ALD processes. For these reasons, new precursor chemistry needs to be developed. Another factor in the precursor chemistry of oxide film growth is the choice of the oxygen source, which can strongly affect the resulting properties, e.g., by providing films with reduced impurity levels and better electrical characteristics.[13,14] In this respect, water, a commonly used oxygen source, can be replaced by a more aggressive oxidant, viz. ozone.

Here, we wish to introduce volatile, reactive, thermally stable, and liquid cyclopentadienyl-type precursors for the controlled growth of HfO_2. In total, four new Cp-precursors, namely, $(CpMe)_2HfMe_2$, $Cp_2Hf(OMe)_2$, $(CpMe)_2Hf(OMe)Me$, and $(CpMe)_2Hf(OMe)_2$, are studied. To obtain the best possible film properties, we used ozone as the oxygen source. Cp-precursors have been successfully employed in ALD, e.g., for noble metals,[2,15] but for Zr and Hf, the Cl-free Cp-compounds tested so far, Cp_2ZrMe_2 and Cp_2HfMe_2, are solid and show thermal decomposition in the gas phase at around 400 °C.[16−19] Considering the extensive chemistry of cyclopentadienyl-type compounds and our previous encouraging results, we have chosen the Cp_2HfMe_2 as a base material and made some carefully considered synthetic modifications to improve its behavior as an ALD precursor.

Experimental Section

Synthesis of the Precursors. The Hf-cyclopentadienyl precursors were synthetized by a modified method described previously[20,21] and are listed in Table 1, where selected properties relevant for ALD growth are also shown. All manipulations were performed under dry nitrogen gas using standard Schlenk techniques. Solvents were purified by distillation under nitrogen from sodium (hexane) or sodium-benzophenone (Et_2O, toluene). $HfCl_4$ and $Hf(NMe_2)_4$ (Aldrich) were used without further purification. *n*-BuLi (1.6 M in hexane), MeLi (1.6 M in diethyl ether), and methanol were purchased from Aldrich. Methylcyclopentadiene monomer was obtained by cracking its dimer at about 200 °C and collecting at a temperature range of 90−100 °C. C_6D_6 was degassed and dried over activated 4 Å molecular sieves before use. NMR (^1H) spectra were recorded on a Bruker 250 spectrometer, and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts were referenced to residual solvent C_6D_6 peaks (^1H at 7.15 and ^{13}C at 128 ppm). Thermal analysis was carried out in a thermogravimetric analyzer (Shimadzu TGA-51), and vapor pressures were recorded on a vapor pressure measurement system (MKS Instruments).

Synthesis of $(CpMe)_2HfMe_2$. Methylcyclopentadiene monomer (102.4 g, 1.28 mol) was dissolved in diethyl ether (300 cm^3) and slowly added to a stirred hexane solution of *n*-BuLi (800 cm^3, 1.28 mol, 1.6 M in hexane) at ∼15 °C with the formation of a white precipitate. Following the addition of the methylcyclopentadiene solution, the reaction mixture was stirred for 1 h at room temperature.

The reaction mixture was then cooled to 0 °C, and solid hafnium chloride (205 g, 0.64 mol) was added. Following the addition of hafnium chloride, the reaction mixture was stirred at room temperature for 2 h. To the resultant reaction mixture was added a diethyl ether solution of methyl lithium (1.28 mol, 800 cm^3, 1.6 M in diethyl ether) at 20 °C. This was then stirred for 2 h at room temperature, after which the solids were removed by filtration. Volatiles were removed in vacuo followed by vacuum distillation (125 °C at 1.7−2.2 mmHg) to yield a semisolid colorless product, 162.0 g (69.2%). Microanalysis. Found: C, 45.50; H, 5.40.; Calcd for $C_{14}H_{20}Hf$: C, 45.80; H, 5.45.

^1H NMR (C_6D_6, δ): 0.40 (s, 6H, $HfCH_3$); 2.00 (s, 6H, CH_3Cp); 5.45 (m, 4H aromatic protons in Cp ring); 5.57 (m, 4H aromatic protons in Cp ring).

^{13}C NMR (reference to C_6D_6 at 128 ppm): 121.57, 111.51, 111.34, 107.22, 107.3, 36.36, 15.15.

ICP−MS: $[Cl^-] = 15$ ppm, $[Li] = 1.1$ ppm, $[Zr] = 200$ ppm, $[Ti] = 0.04$ ppm.

Thermostability at 200 °C: longer than 50 h.

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Synthesis of (CpMe)$_2$Hf(OMe)Me. Methanol (9.0 g, 0.28 mol) dissolved in hexane (100 cm^3) was added slowly with stirring at a temperature of 20 °C to (CpMe)$_2$HfMe$_2$ (100.0 g, 0.27 mol), which was also dissolved in hexane (500 cm^3). The reaction mixture was then stirred for 3 h. The volatiles were removed in vacuo followed by vacuum distillation (105 °C at 0.3−0.4 mmHg) to give a colorless liquid, 81.4 g (78.9%). Microanalysis. Found: C, 43.53; H, 5.24. Calcd for $C_{14}H_{20}OHf$: C, 43.93; H, 5.27.

^{1}H NMR (C_6D_6, δ): 0.09 (s, 3H, HfCH_3); 1.95 (s, 6H, CH_3Cp); 3.69 (s, 3H, OCH_3); 5.50−5.60 (m, 8H aromatic protons in Cp ring). ^{13}C NMR: 112.57, 112.16, 108.90, 107.75, 107.18, 60.15, 21.55, 14.56.

ICP−MS: [Cl$^-$] < 5 ppm, [Li] = 0.01 ppm, [Zr] = 24.3 ppm, [Ti] <0.01 ppm.

Thermostability at 200 °C: longer than 50 h.

Synthesis of Cp$_2$Hf(OMe)$_2$. Freshly cracked cyclopentadiene monomer (21.9 g, 0.33 mol) was added to a stirred solution of hafnium dimethylamide (57.8 g, 0.16 mol) dissolved in toluene (500 cm^3). The reaction mixture was then refluxed for 2 h. Proton NMR on the reaction mixture showed the reaction to be incomplete; therefore, additional cyclopentadiene (20.0 g, 0.30 mol) was added followed by a further 2 h reflux. Removal of the volatiles in vacuo gave Cp$_2$Hf(NMe$_2$)$_2$ as a yellow/brown solid, 60.2 g (94.8%).

Cp$_2$Hf(NMe$_2$)$_2$ (30.7 g, 0.08 mol) was dissolved without further purification in toluene (250 cm^3) to which methanol (4.8 g, 0.15 mol) was slowly added with stirring. The resulting reaction mixture was then refluxed for 2 h and the volatiles removed in vacuo to give a dark brown oil. Further drying of the oil in vacuo gave a dark brown highly viscous oil, which was then extracted into toluene and filtered. The solvent was then removed in vacuo and the final product obtained was white crystals by vacuum sublimation (60−70 °C at 0.5 mmHg), 21.5 g (75.5%). Microanalysis. Calcd: C, 41.95; H, 5.53. Found: C, 40.93; H, 4.95.

^{1}H NMR (C_6D_6, δ): 3.85 (s, 6H, Hf(OCH_3)$_2$); 5.94 (s, 10H aromatic protons in Cp ring). ^{13}C NMR: 110.29, 109.28, 60.20, 14.85.

Synthesis of (CpMe)$_2$Hf(OMe)$_2$. Methylcyclopentadiene monomer (61.4 g, 0.77 mol) was added to a stirred solution of hafnium dimethylamide (45.1 g, 0.13 mol) dissolved in toluene (500 cm^3) following the methodology described above. Drying of the brown solid product in vacuo gave (CpMe)$_2$Hf(NMe$_2$), 50.4 g (91.4%).

(CpMe)$_2$Hf(NMe$_2$) (35.0 g, 0.08 mol) was dissolved without further purification in toluene (250 cm^3) to which methanol (5.1 g, 0.16 mol) was slowly added with stirring following the procedure described previously. Crystallization of the dark highly viscous oil from cold hexane gave white crystals of (CpMe)$_2$Hf(OMe)$_2$, 20.5 g (62.4%). Microanalysis. Calcd: C, 38.88; H, 4.35. Found: C, 39.15; H, 4.40.

^{1}H NMR (C_6D_6, δ): 2.02 (s, 6H, CH_3Cp); 3.88 (s, 6H, Hf(OCH_3)$_2$); 5.61 (m, 4H aromatic protons in Cp ring); 5.69 (m, 4H aromatic protons in Cp ring).^{13}C NMR: 111.27, 60.68.

HfO$_2$ Film Deposition. Thin films depositions were carried out onto p-type Si(100) substrates measuring 10 × 5 cm^2. Immediately prior to the depositions, some of the substrates were etched in hydrofluoric acid (HF, 2%) for 2 min in order to remove the native SiO$_2$. Native oxide covered Si substrates were ultrasonically cleaned in ethanol and distilled water.

HfO$_2$ thin films were deposited in a commercial flow-type hot-wall atomic layer deposition reactor (F-120 by ASM Microchemistry Ltd.) using different hafnium cyclopentadienyl compounds as metal sources. Ozone was used as oxygen source, but for some depositions distilled water was used. O$_3$ was generated from O$_2$ (99.999%) in an ozone generator (Fischer model 502). Nitrogen (>99.999%, Schmidlin UHPN 3000 N$_2$ generator) was used as a carrier and purging gas. Thin film depositions were carried out under a 2−3 mbar pressure. Hafnium precursors were evaporated from open glass crucibles at temperatures ranging from 60 to 65 °C (Table 1).

Film Characterization Methods. Reflectance and transmittance spectra were measured in a double beam spectrophotometer (Hitachi U-2000). The obtained reflectance data were used for calculating thicknesses of the deposited films using the method described by Ylilammi and Ranta-aho.[22] Thickness, roughness, and density of thinner HfO$_2$ films were evaluated by X-ray reflectometry (XRR, Bruker D8 Advance X-ray diffractometer). Crystallite orientations and crystallinity of the deposited films were determined by X-ray diffraction (Philips MPD 1880 diffractometer) with Cu K$_\alpha$ radiation.

The stoichiometry and possible impurities of HfO$_2$ thin films were measured using Rutherford backscattering spectroscopy (RBS) and time-of-flight elastic recoil detection analysis (TOF-ERDA)[23,24] as well as Auger electron spectroscopy (AES). AES was carried out on a scanning Auger spectrometer (Varian Instruments). The atomic compositions quoted are from the bulk of the films, which are free from surface contamination and were obtained by combining AES with sequential argon ion bombardment until comparable compositions were obtained for consecutive data points. Compositions were based on HfO$_2$ powder reference materials.

For electrical characterization, aluminum gate electrodes with an effective area of 0.204 mm^2 and thickness of 100 nm were e-beam evaporated through a shadow mask onto the HfO$_2$ film surface. The backsides of the substrates were HF-etched prior to the deposition of continuous aluminum electrode in order to create ohmic contacts. Al/HfO$_2$/HF-etched p-Si(100)/Al capacitor structures thus created were measured with a precision LCR meter (HP 4284A) and source meter (Keithley 2400) to obtain capacitance−voltage ($C-V$) and current−voltage ($I-V$) characteristics, respectively. All electrical measurements were carried out at room temperature. For the $C-V$ measurements, the voltage step was 0.05 V and the frequency of the ac signal was 500 kHz. For the $I-V$ measurements, stair sweep voltage with a step of 0.05 V was applied.

Results and Discussion

As shown in Table 1, the Cp compounds, except for Cp$_2$Hf(OMe)$_2$, are liquids at low temperatures at the reduced ALD reactor pressure of 2−3 mbar. Cp$_2$Hf(OMe)$_2$ is partly liquid at the evaporation temperature. These precursors are volatile enough to be used in ALD and no decomposition during evaporation is observed, as shown by the thermogravimetric (TG) curves measured at atmospheric pressure (Figure 1). Vaporization generally occurs in a single step with low residual mass. Nevertheless, the residual mass for Cp$_2$Hf(OMe)$_2$ and (CpMe)$_2$Hf(OMe)$_2$ is significant or about 15%.

As expected from the TG measurements, (CpMe)$_2$HfMe$_2$ and (CpMe)$_2$Hf(OMe)Me show the highest potential for the actual film growth. In Figure 2a, the growth rate of HfO$_2$ film is shown as a function of deposition temperature, obtained by the (CpMe)$_2$HfMe$_2$/O$_3$ and (CpMe)$_2$Hf(OMe)Me/O$_3$ processes. The growth rate remains quite constant

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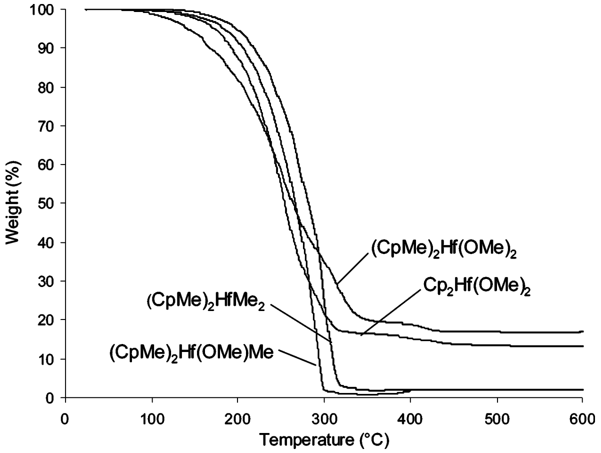

Figure 1. TG curves for the Hf-cyclopentadienyl compounds at atmospheric pressure.

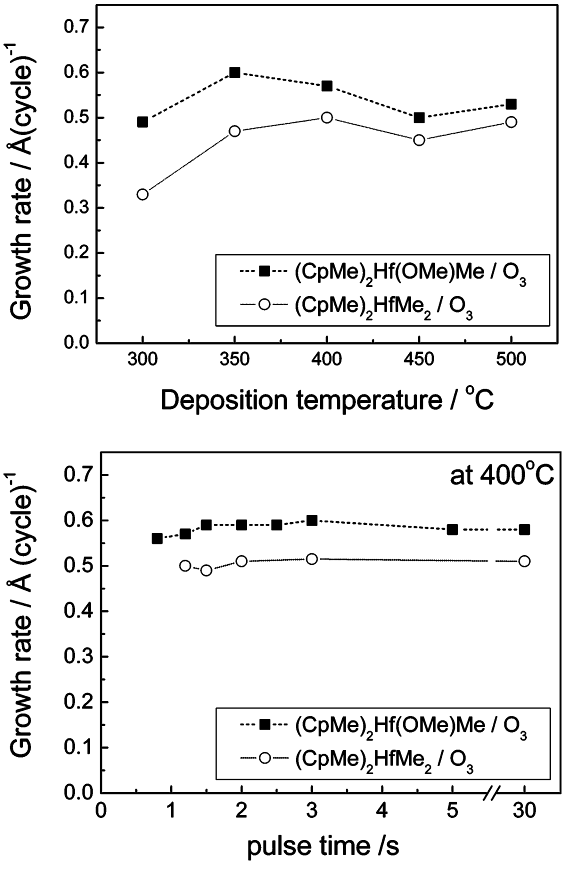

Figure 2. The growth rate of HfO_2 thin films from (CpMe)$_2$Hf(OMe)Me/O_3 and (CpMe)$_2$HfMe$_2$/O_3 as a function of the (a) deposition temperature and (b) metal precursor pulse time.

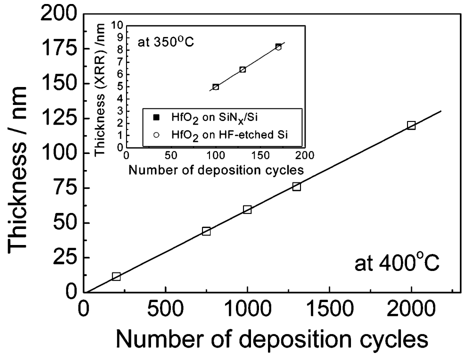

Figure 3. The dependence of HfO_2 film thickness on the number of deposition cycles. HfO_2 grown by the (CpMe)$_2$Hf(OMe)Me/O_3 process at 400 or 350 °C (inset).

over a wide temperature range, around 0.5 Å/cycle for the (CpMe)$_2$HfMe$_2$/O_3 and slightly higher for the (CpMe)$_2$Hf(OMe)Me/O_3. It is quite interesting to note that both processes produce perfectly uniform films regardless of the deposition temperature between 300 and 500 °C. The self-limiting, saturative growth behavior was confirmed by a greater than 20-fold increase in the (CpMe)$_2$HfMe$_2$ and (CpMe)$_2$Hf(OMe)Me pulsing time up to 30 s, without any increase in the observed deposition rate or decrease in the film uniformity at the deposition temperature of 400 °C (Figure 2b). Excellent thermal stability even at the growth temperature of 450 °C was realized, whereas the growth rate remained constant with a 30 s metal precursor pulse duration. It should be noted that replacing ozone by water as the oxygen source yielded growth rates of about 0.1 Å/cycle lower at every temperature. At these substantially high deposition temperatures, the reactivity of H_2O is sufficient toward hafnium cyclopentadiene compounds. Previously, we have observed low reactivity of Cp_2HfMe_2 toward water at 300 °C.[18] Slightly higher growth rate values of around 0.6−0.7 Å/cycle were obtained for the $Cp_2Hf(OMe)_2/O_3$ and (CpMe)$_2$Hf(OMe)$_2$/O_3 processes. When self-limiting growth for these two processes was studied by increasing the metal precursor pulsing time at 350−400 °C, a slight decomposition of the precursors was observed. This was seen in the approximately 5% increase in the growth rate at the leading edge of the substrates when pulsing time was increased from 1.0 to 2.0 s. On the basis of these results, more extensive deposition tests for these two precursors were discontinued.

Previously, we have studied the growth behavior of zirconia by in situ analysis of the Cp_2ZrMe_2/H_2O process at 200−450 °C.[17] For both the Cp_2ZrMe_2 and Cp_2HfMe_2 precursors, thermal decomposition around 400 °C was observed. Typically the metal to C_5H_5−ligand bond has been observed to break at higher temperatures, viz. above 400 °C, and therefore self-limiting ALD growth has not been obtained.[17,18] In addition, thermal gas-phase decomposition of aromatic ligands is reported to start around 450−520 °C.[25,26] In this respect, a self-limiting growth and almost constant deposition rate up to 500 °C is quite a remarkable result, offering great prospects for industrial applications. It seems that the introduction of the unsymmetric −OMe/−Me ligands and slightly more bulky CpMe−ligand into the cyclopentadiene compounds of hafnium significantly enhances their thermal stability.

A perfectly linear dependency of film thickness on the number of cycles, characteristic for an ALD process, was observed when HfO_2 was deposited on silicon at 400 °C by using (CpMe)$_2$HfMe$_2$ (Figure 3) or (CpMe)$_2$Hf(OMe)Me. When ultrathin films (<10 nm) were deposited at 350 °C by the (CpMe)$_2$Hf(OMe)Me/O_3 process on SiN$_x$ or HF-terminated Si substrates, a slightly lower deposition rate of 0.5 Å/cycle was measured by XRR (Figure 3, inset), whereas

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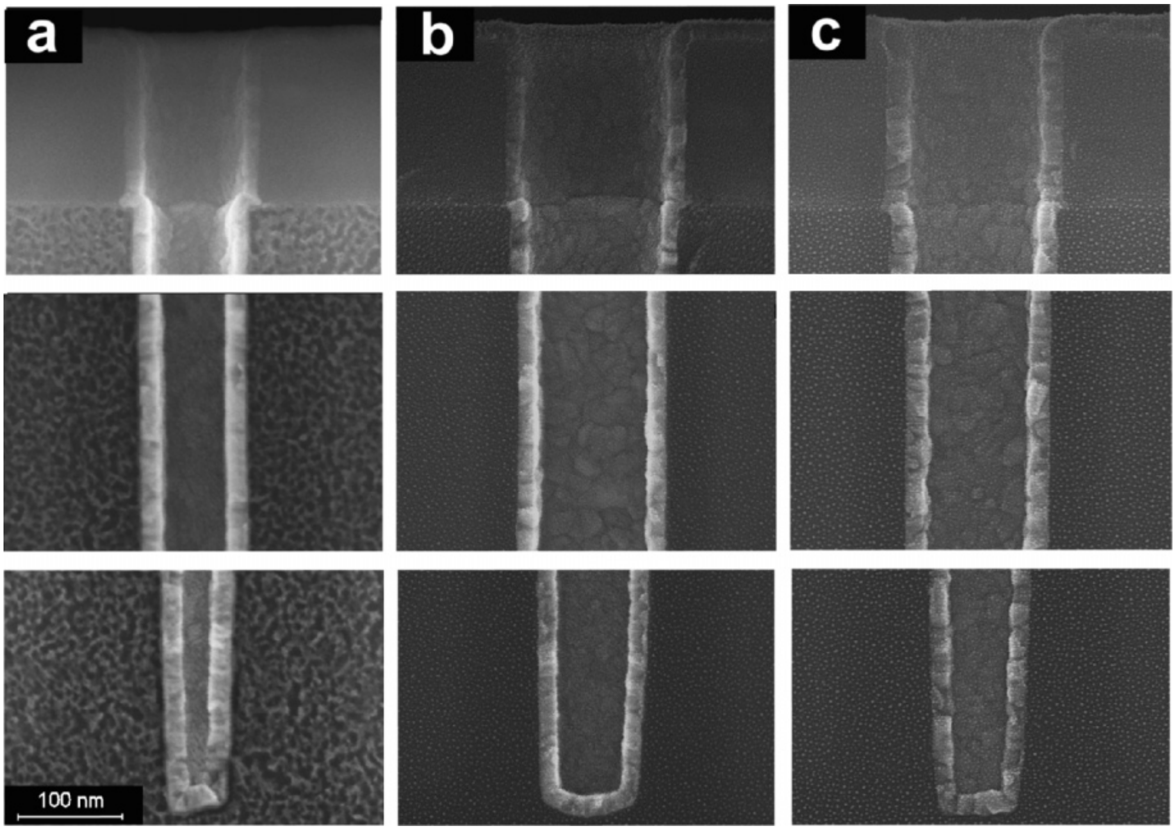

Figure 4. High-resolution SEM images of a cross-section of a deep trench with 20 nm HfO_2 deposited by (a) a $(CpMe)_2HfMe_2/O_3$ process at 400 °C and by a $(CpMe)_2Hf(OMe)Me/O_3$ process at (b) 400 and (c) 450 °C. Trench aspect ratio is ~60:1 with 6.75 μm depth and 115 nm opening. The upper images show the top part of the trenches, those below show the middle and the bottom at a depth of 6.75 μm.

the linear dependency was maintained. This difference in growth rates can be attributed to the different initial growth surfaces and different methods of film thickness determination. According to the XRR measurements, the density of 5−10 nm thick HfO_2 thin films grown at 350−450 °C on native-oxide-covered Si, H-terminated Si, and SiN_x/Si substrates was around 9.9−10.7 g/cm^3, close to the stoichiometric bulk value.

To check the conformality of the deposited HfO_2 films, we carried out some test depositions onto trenched wafers with an aspect ratio of 60:1. Both $(CpMe)_2HfMe_2/O_3$ and $(CpMe)_2Hf(OMe)Me/O_3$ processes were employed at 350−450 °C. A 30 s pulse time was used for the hafnium precursors and ozone in order to ascertain that there is enough time for precursors to diffuse to the bottom of the 6.75 μm deep trench. Initially, 40 s purge times were used between the reactive pulses. According to the cross-sectional SEM images, all films were uniform up to the deposition temperature of 450 °C (Figure 4). If decomposition of the precursor and thus a CVD-type growth mode would be present, severe thickness profiles should be clearly visible. In the present case, the conformality is nearly perfect in spite of the high deposition temperature used. In some samples, certain overconformality (where thickness at the bottom of the trench is about 5−10% larger than that on the top) was observed for these approximately 20 nm thick films because of too short a purge time. This could be eliminated by increasing purge times up to, for example, 60 s. If depositions were carried out at 450 °C, increased grain size was observed. When comparing the current Cp-based process to the alkylamide-based processes, about a 200 °C higher temperature can be used for the HfO_2 trench DRAM depositions, which certainly is a significant improvement.[10,11]

XRD measurements were performed for the HfO_2 thin films having a thickness of 50−70 nm. Regardless of the hafnium precursor used, films were polycrystalline monoclinic HfO_2 with the (−111) reflection as the strongest one. At lower temperatures, intensities of the reflections were weak and full width at half-maximum (fwhm) values were relatively high, indicating low crystallinity. However, crystallinity of the HfO_2 films was increased when the deposition temperature was increased from 300 to 500 °C. At the same time, fwhm values were decreased, confirming an increase in the film crystallinity. A similar increase in film crystallinity has been observed in the HfO_2 films deposited by the Cp_2HfMe_2/O_3 process.[18]

Stoichiometry and impurity levels of HfO_2 films were examined by TOF-ERDA (Table 2), RBS and AES for films deposited onto Si(100) substrates at 350−450 °C. In general, impurity levels were very low and were independent of the deposition temperature. Both carbon and hydrogen contents were below the detection limit (0.1 at % for C and H determination by TOF-ERDA and 1 at % for carbon determination by AES) for films deposited from all four Hf-precursors. Other impurities, such as Cl or N, were not detected. Diminutive amounts (about 0.1 at % or less) of Zr, a common impurity in Hf precursors, were detected, however. According to the compositional analysis, the hafnium to oxygen ratio was stoichiometric in all samples. These results agree well with the previous ones obtained with

Table 2. Elemental Composition of HfO_2 Films as Determined by TOF-ERDA

		area density (1×10^{16} at/cm^2)			
precursors used	T_{growth} (°C)	O	Hf	C, H, N, Cl at %	Hf/O ratio
$(CpMe)_2HfMe_2/O_3$	350	33.7	16.9	<0.1	0.50
	400	42.0	20.6	<0.1	0.49
$Cp_2Hf(OMe)_2/O_3$	350	31.2	14.7	<0.1	0.47
$(CpMe)_2Hf(OMe)Me/O_3$	350	31.2	16.0	<0.1	0.51
	400	30.8	14.4	<0.1	0.47
	450	29.1	14.1	<0.1	0.48
$(CpMe)_2Hf(OMe)_2/O_3$	350	34.0	17.1	<0.1	0.50

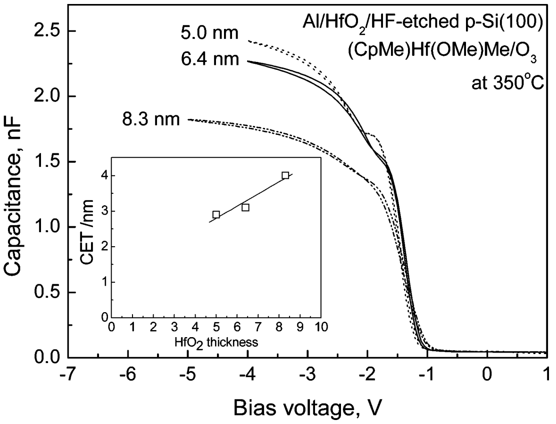

Figure 5. Capacitance−voltage curves of Al/HfO_2/HF-etched p-Si(100) capacitor structures with HfO_2 film grown at 350 °C using the $(CpMe)_2Hf(OMe)Me/O_3$ process. Labels indicate the HfO_2 thickness as characterized by XRR. Inset shows the capacitance equivalent oxide thickness (CET) as a function of the HfO_2 film thickness.

the Cp_2HfMe_2/O_3 process.[19] It is interesting to note that although there is slightly more carbon in the precursors than in Cp_2HfMe_2, it does not affect the impurity levels of the deposited films. It seems that O_3 being a strong oxidizer can effectively burn off the possible carbon impurities.

Typical capacitance−voltage (*C*−*V*) curves for the Al/HfO_2/HF-etched/p-Si(100)/Al structures, where the HfO_2 layer was deposited by the $(CpMe)_2Hf(OMe)Me/O_3$ process at 350 °C, are shown in Figure 5. Effective permittivities (that is, where the contribution of the interfacial layer is taken into account) of around 8−9 were obtained for the 5−10 nm thick HfO_2. These effective permittivity values are similar to those in the case of Cp_2HfMe_2/O_3[19] but better than those observed for the $Hf(NEtMe)_4/H_2O$, where a relatively thin film was deposited on H-terminated Si.[27] Low hysteresis with some flat-band voltage (V_{FB}) shift (<0.5 V), indicative of the presence of some positive fixed charge, was also observed. The hysteresis and the V_{FB} voltage shift values are also in good agreement with the values previously measured for films deposited by the Cp_2HfMe_2/O_3 process on H-terminated Si.[19] It should be noted here that the "shoulder" feature seen in the *C*−*V* curve depletion regime near the flat-band voltage originates from the silicon dangling bonds and can be minimized by annealing.[28] If the calculated capacitance equivalent oxide thickness (CET) values are plotted against the physical film thickness, permittivity values of around 12 can be calculated from the slope. Interfacial layer thickness of around 1.0 nm can also be estimated. The leakage current density at $V_{FB} - 1$ V was typically around 1×10^{-7} A/cm.

Conclusions

We conclude that the ALD growth of high-quality HfO_2 thin films was successfully achieved from novel organometallic hafnium precursors, namely, $(CpMe)_2HfMe_2$ or $(CpMe)_2Hf(OMe)Me$ with either ozone or water as the oxygen source. A self-limiting HfO_2 deposition, including coating of high-aspect-ratio trenches with perfect conformality, was observed for the $(CpMe)_2HfMe_2/O_3$ or $(CpMe)_2Hf(OMe)Me/O_3$ processes even up to 450−500 °C, which is a remarkably high growth temperature regime for processes employing organometallic cyclopentadienyl-based precursors. In addition, both $Cp_2Hf(OMe)_2/O_3$ and $(CpMe)_2Hf(OMe)_2/O_3$ processes afforded a reasonable deposition rate of about 0.7 Å/cycle, but they showed some precursor decomposition at 350 °C. However, their thermal stability was not evaluated at lower temperatures. Deposition temperature shift from 350 to 500 °C had only a minor effect on the growth rates of the HfO_2 film deposited by the $(CpMe)_2HfMe_2/O_3$ or $(CpMe)_2Hf(OMe)Me/O_3$ processes. Saturation of the growth rate as a function of reactive pulses even with a 20-fold increase in Hf precursor pulse times together with linear dependency of film thickness as a function of the number of deposition cycles indicate a well-controlled ALD-type growth even at 450 °C. According to TOF-ERDA, RBS, and AES results, stoichiometric HfO_2 films with no detectable impurities were obtained with all precursors; e.g., the $(CpMe)_2Hf(OMe)_2/O_3$ process at 350−450 °C yielded films with impurity levels below the detection limit of TOF-ERDA (0.1 at %). The liquid cyclopentadienyl compounds of hafnium introduced herein thus offer a feasible industrial solution for the high-*k* HfO_2 growth by ALD for gate dielectric and especially for trench DRAM capacitor applications in which extreme conformality, purity, and uniformity are required.

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