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Chemical Vapor Deposition of HfO_2 Thin Films Using the Novel Single Precursor Hafnium 3-Methyl-3-pentoxide, $Hf(mp)_4$

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Hafnium oxide films have been deposited on silicon substrates by metal organic chemical vapor deposition using the novel single precursor, hafnium 3-methyl-3-pentoxide $\{Hf[OC(CH_3)(C_2H_5)_2]_4$, $Hf(mp)_4\}$, with no additional oxygen source, and the deposition mechanism was elucidated. $Hf(mp)_4$ is a liquid at room temperature and has a moderate vapor pressure comparable to that of hafnium *tert*-butoxide, $Hf(O^tBu)_4$, and a lower residual weight ($<10\%$) in thermogravimetric analysis. The deposition rate was found to be ∼27 Å/min at 400 °C, and the activation energy was 68.1 kJ/mol, which is higher than those of other hafnium alkoxide and hafnium amide precursors. By gas chromatography/mass spectroscopy and nuclear magnetic resonance analyses of the thermally decomposed vapor phase products collected during the deposition of HfO_2 films, it was clearly found that they are grown via β-hydrogen elimination processes of the $Hf(mp)_4$ single precursor. Negligible carbon incorporation of the HfO_2 films, examined by X-ray photoelectron spectroscopy and depth-profiling Auger electron spectroscopy, indicates that, except for the β-hydrogen elimination processes, no additional decomposition and/or recombination processes contributed to the HfO_2 film growth. The morphology, crystallinity, and electrical properties of the HfO_2 films were characterized by scanning electron microscopy, atomic force microscopy, X-ray diffraction, and capacitance−voltage and current−voltage measurements.

Introduction

The material of choice for gate dielectrics has been thermally grown silicon dioxide (SiO_2) due to its excellent insulator properties, low defect densities, and thermal stability. Unfortunately, however, the use of SiO_2 and SiO_xN_y as gate dielectrics is reaching the fundamental limits primarily due to high leakage currents below the gate oxide thickness of ∼2 nm.[1]

Hafnium dioxide (HfO_2) has been extensively studied for use as a replacement for SiO_2 in the gate oxide insulating layer in complementary metal oxide semiconductor (CMOS) devices.[2] Considerable attention has been given to HfO_2 due to its relatively high dielectric constant (16−40),[3,4] wide band gap (∼5.68 eV),[5] and thermodynamic stability up to ∼1000 K.[6,7]

Among many possible deposition techniques, chemical deposition methods, such as metal organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD), have been mainly employed for high-quality HfO_2 films because of the thickness uniformity over large-area substrates, control of interfaces, film homogeneity, and accurate stoichiometry. In both CVD and ALD, the selection of proper precursors is essentially important. A great number of Hf precursors have been examined during the past years, such as hafnium β-diketonates [$Hf(tfac)_4$,[8] tfac = trifluoroacetylacetonate, and $Hf(acac)_4$,[9] acac = acetylacetonate], hafnium alkoxides [$Hf(O^tBu)_4$,[10−14] $Hf(mmp)_4$,[15] mmp = 1-methoxy-

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2-methyl-2-propanolate, Hf(dmae)$_4$,[16] dmae = dimethylaminoethoxide, and Hf$_3$(μ_3-O)(μ_3-ONep)(μ-ONep)$_3$(ONep)$_6$[17]], hafnium mixed alkoxides [Hf(O^{i}Pr)$_2$(tbaoac)$_2$,[18] tbaoac = *tert*-butylacetoacetato, and Hf(O^{t}Bu)$_2$(mmp)$_2$[19]], hafnium amides [Hf(NMe$_2$)$_4$, Hf(NEt$_2$)$_4$, and Hf(NMeEt)$_4$],[20−25] anhydrous hafnium nitrate [Hf(NO$_3$)$_4$],[26] hafnium tetrachloride [HfCl$_4$],[27,28] etc. Although HfCl$_4$ has been used for the ALD of HfO$_2$ films, it is a solid at room temperature, induces chlorine contamination, and produces the highly corrosive hydrochloric acid. Hf(NO$_3$)$_4$ has handling problems because it is also a solid at room temperature and extremely reactive. Moreover, an interfacial silicon oxide layer is formed on a Si substrate surface by oxidation during deposition. Hafnium amides have low decomposition temperatures and tend to produce particles on the growing films due to premature gas-phase reactions. Hafnium alkoxides can be used without an additional oxygen source such as water, ozone, or molecular oxygen. Especially, Hf(O^{t}Bu)$_4$ is the main single precursor currently in use for MOCVD of HfO$_2$ films. Hf(O^{t}Bu)$_4$ is a liquid at room temperature and has a relatively high vapor pressure providing both hafnium and oxygen by itself. However, Hf(O^{t}Bu)$_4$ is very reactive and easily undergoes a catalytic hydrolytic decomposition reaction in the presence of trace water[29] and, therefore, has a short shelf life. It causes clogging of the supply lines of the deposition chamber. Additionally, in the single source MOCVD of HfO$_2$ films, Hf(O^{t}Bu)$_4$ leaves some level of carbon incorporation, probably because there is no well-defined decomposition process. In actual fact, it leaves a large residue of almost 30% of the original weight in thermogravimetric analysis.

In this work, hafnium oxide films were deposited on silicon substrates by MOCVD using the newly employed novel single precursor hafnium 3-methyl-3-pentoxide, {Hf[OC(CH$_3$)(C$_2$H$_5$)$_2$]$_4$, Hf(mp)$_4$}, without an extra oxygen source. This precursor has the ligand (mp) bulkier than *tert*-butoxide, which effectively lowers the reactivity of the precursor but not to such an extent that the stabilization hinders its reactivity as an MOCVD source. The reaction mechanism was clearly identified by the analysis of its thermal decomposition. The properties of the Hf(mp)$_4$ single precursor were compared with other hafnium alkoxide precursors. The deposition characteristics were investigated together with the composition, crystallinity, and electrical properties of the deposited films.

Experimental Section

Synthesis and Characterization of the Precursor. A solution of 3-methyl-3-pentanol (mpH: 4.37 g, 47.1 mmol) dissolved in hexane (30 mL) was slowly added to a solution of Hf(NEt$_2$)$_4$ (5.00 g, 10.7 mmol) in hexane (50 mL) at room temperature. The reaction mixture was stirred for 12 h, and the volatiles were removed in vacuo. Finally, a pure yellow liquid Hf(mp)$_4$ was obtained by distillation at 130 °C under a reduced pressure (yield 6.13 g, 98.2%). The structure of the precursor was confirmed by nuclear magnetic resonance (NMR) spectroscopy. ^{1}H NMR (C$_6$D$_6$, 300.13 MHz): δ 1.03 (t, 24H, *J* = 7.5 Hz, CCH$_2$C*H*$_3$), 1.22 (s, 12H, CC*H*$_3$), 1.54 (q, 16H, *J* = 7.5 Hz, CC*H*$_2$CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.03 MHz): δ 79.9 (O*C*CH$_3$), 35.6 (C(*C*H$_2$CH$_3$)$_2$), 27.5 (C*C*H$_3$), 8.80 (C(CH$_2$*C*H$_3$)$_2$). Elemental analysis for C$_{24}$H$_{52}$O$_4$Hf. Calcd, C, 49.43, H, 8.99. Found, C, 49.87; H, 9.20. The precursor Hf(mp)$_4$ is a liquid at room temperature and has a moderate vapor pressure (0.31 Torr at 65 °C). To investigate its thermal stability, we conducted ^{1}H NMR tests of the precursor remaining after a series of 10−15 depositions, which lasted about 3 days. It was always found that the ^{1}H NMR spectrum of the remaining precursor in the source vessel was identical with that of the original Hf(mp)$_4$.

Growth of HfO$_2$ Thin Films and Thermal Decomposition of the Precursor. A horizontal, stainless steel, low vacuum chamber was used to grow the HfO$_2$ films. The distance from the doser tip to the substrate surface was ∼30 mm. The substrates were p-type Si(001) wafers. Before it was placed in the reactor, a substrate was etch-cleaned in a dilute hydrofluoric acid (HF) to remove the native oxide formed on the surface and then rinsed with deionized water. The substrate temperature was varied in the range 300−600 °C. The base pressure of the deposition chamber was 3×10^{-2} Torr and the pressure increased to 2×10^{-1} Torr during the film growth without any carrier or reactant gas. The precursor vessel was placed in an oil bath that was maintained at 120 °C. The temperatures of all dosing lines were about 125 °C.

To identify the thermal decomposition products of Hf(mp)$_4$, the precursor was passed through a quartz tube that was packed with many pieces of Si wafers and kept at 400 °C. The vapor phase reaction products were collected in a liquid nitrogen trap placed before the exhaust, and analyzed by using GC/MS and ^{1}H NMR spectroscopy.

Characterization of the HfO$_2$ Thin Films. The thicknesses of the HfO$_2$ films were measured by an ellipsometer using a He−Ne laser and some of the measurements were compared with cross-sectional scanning electron microscopy (SEM) images. The surface morphology of the films was characterized by SEM and atomic force microscopy (AFM, Nanoscope IV, Digital Instrument), for which a silicon tip with a 10-nm radius of curvature was used in the tapping mode. Chemical compositions and impurities of the films were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB MK II, VG Scientific, Ltd., using the Mg K$\alpha_{1,2}$ radiation with the energy 1253.6 eV) after Ar ion sputtering and depth-profiling Auger electron spectroscopy (AES). X-ray diffraction (XRD) with the Cu Kα radiation (λ = 1.541838 Å) was employed to investigate the crystallinity of the films. Dielectric properties were measured after e-beam evaporation of aluminum (Al) through a shadow mask to deposit dot electrodes with the effective area of

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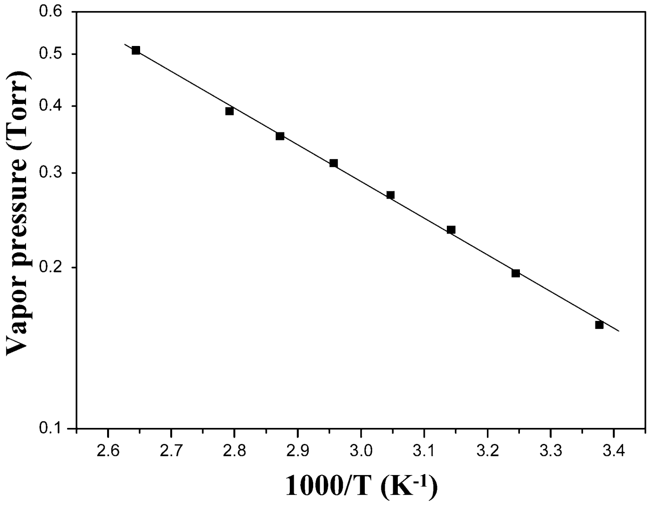


Figure 1. Vapor pressure of $Hf(mp)_4$ in the temperature range 23−105 °C.

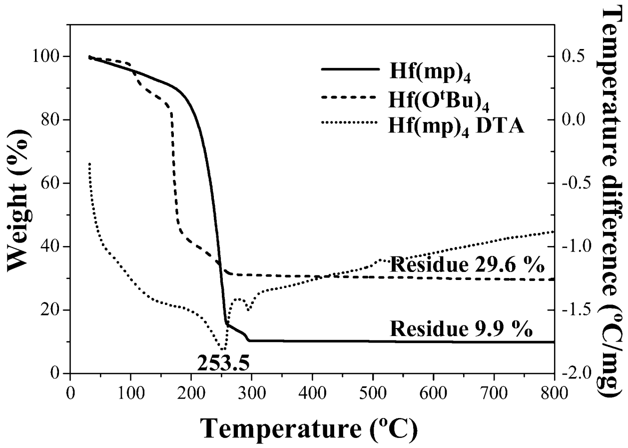


Figure 2. TG/DTA curves of $Hf(mp)_4$ obtained in a N_2 atmosphere with the heating rate of 10 °C/min.

3.14×10^{-4} cm^2 on the surface of a HfO_2 film. The capacitance−voltage (C−V) characteristics were analyzed at 1 MHz using a HP 4192A impedance spectroscopy analyzer with a sweep voltage ranging from −6 to +6 V. The current−voltage (I−V) measurements were performed with a Keithley 6517A multimeter to investigate the breakdown strength and the leakage current through the oxide film.

Results and Discussion

Characterization of the Precursor. The vapor pressure of $Hf(mp)_4$ was measured at eight different temperatures (shown in Figure 1), and a typical value is 0.31 Torr at 65 °C. Although this vapor pressure is rather low compared to those of $Hf(O^tBu)_4$ (1.0 Torr at 65 °C)[11] and $Hf(NEt_2)_4$ (1.0 Torr at 80 °C)[21] according to our measurements using a U-tube manometer (we used a diffusion pump oil instead of mercury to increase the accuracy of reading the menisci of the liquid in the U-tube), it is still high enough for obtaining appreciably thick films of HfO_2. The thermal property of $Hf(mp)_4$ was investigated by thermogravimetric and differential thermal analyses (TG/DTA) as shown in Figure 2. TG analysis of the precursor was conducted under a dry nitrogen atmosphere with a 10 °C/min temperature ramp. Upon heating, the $Hf(mp)_4$ precursor underwent a rapid one-step weight loss in the temperature range 170−253.5 °C. The DTA curve shows a main endothermic temperature at 253.5 °C, which is presumably due to the decomposition of $Hf(mp)_4$. A small weight loss was observed above this temperature, beyond which no further weight loss was detected giving the residue below 10% of the starting weight (the amount of this residue was such that no further identification of it could be performed, but in actual CVD processes the precursor vaporized cleanly with no residue left in its container). This fraction is much lower than that of hafnium *tert*-butoxide [$Hf(O^tBu)_4$], which is almost 30%, as shown in Figure 2. The precursor is stable and, in its TGA curve and ^1H NMR spectrum, does not show any sign of degradation even after a prolonged heating at 180 °C (for over 2 weeks). This heating experiment was performed with the $Hf(mp)_4$ precursor in a closed ampule maintained at 180 °C. The precursor was under its own vapor pressure below its boiling point. No decomposition of the precursor was observed; therefore, it was confirmed that the precursor is stable at this temperature.

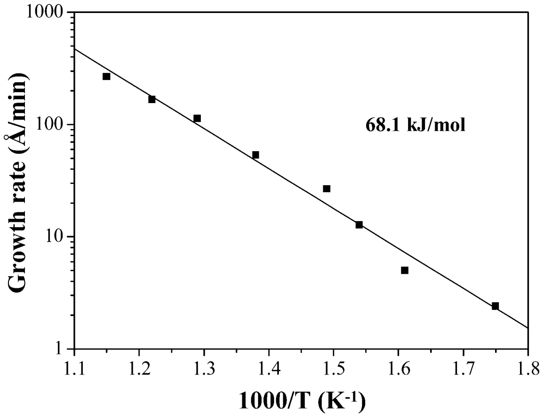


Figure 3. Arrhenius plot for the deposition rates of HfO_2 films on Si substrates.

Characterization of the Films. The deposition rates of the HfO_2 films were measured at various substrate temperatures ranging from 300 to 600 °C. At the convenient growth temperature of 400 °C, the growth rate was found to be ~27 Å/min. Figure 3 shows an Arrhenius plot of the deposition rate as a function of the substrate temperature. The activation energy was calculated at 68.1 kJ/mol, which is much higher than those of $Hf(O^tBu)_4$ (30.4 kJ/mol)[11] and the $Hf(dmae)_4$ (22.2 kJ/mol).[16] This may be explained by the increased stability of the $Hf(mp)_4$ precursor due to the presence of the bulkier ligand mp.

Figure 4 shows the XRD ($\theta-2\theta$) patterns of the HfO_2 thin films deposited at various substrate temperatures. The HfO_2 thin film deposited at 300 °C is amorphous. With the increase of the substrate temperature above 350 °C, the XRD patterns of the films deposited show that the strongest monoclinic phase ($\bar{1}11$) peak develops at $2\theta = 28.36°$ and that the intensities of the monoclinic (020) and (002) peaks are increased for the films deposited at the substrate temperatures of 500−600 °C. These XRD patterns are generally similar to those of the films obtained by using other hafnium alkoxide, $Hf(dmae)_4$,[16] or nitrate, $Hf(NO_3)_4$,[26] precursors.

The AFM image (1.0×1.0 μm^2) of a 4.1-nm-thick HfO_2 film deposited on Si at 400 °C is shown in Figure 5. Its

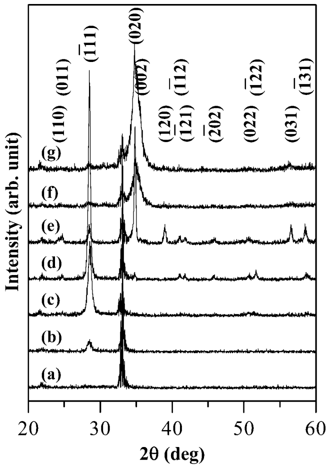


Figure 4. XRD ($\theta-2\theta$) patterns of the HfO_2 films obtained at the substrate temperatures (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 500 °C, (f) 550 °C, and (g) 600 °C.

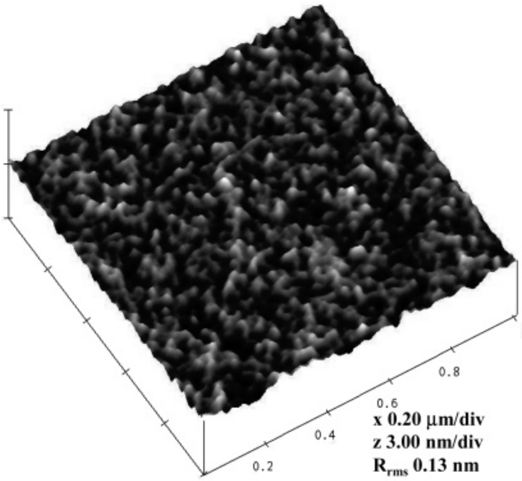


Figure 5. AFM image (1.0 × 1.0 μm^2) of a 4.1-nm-thick HfO_2 film deposited on Si at 400 °C.

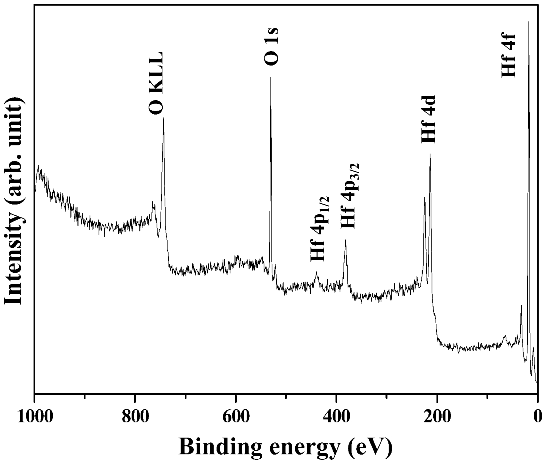


Figure 6. XP survey spectrum of a HfO_2 film deposited on Si at 400 °C.

root-mean-square (rms) roughness was measured to be 0.13 nm, which gives 3.2% for the roughness-to-thickness ratio. This value is comparable to those reported previously for the films grown by other investigators by CVD of hafnium oxoneopentoxide[17] and by ALD of hafnium amide precursors.[22,24] Very smooth HfO_2 films could be deposited from $Hf(mp)_4$ for a wide temperature range.

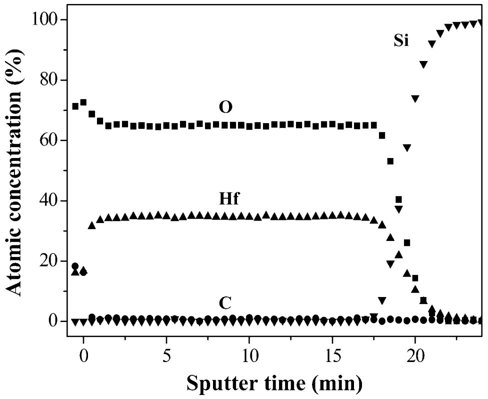


Figure 7. AES depth profile of a HfO_2 film deposited on Si at 400 °C.

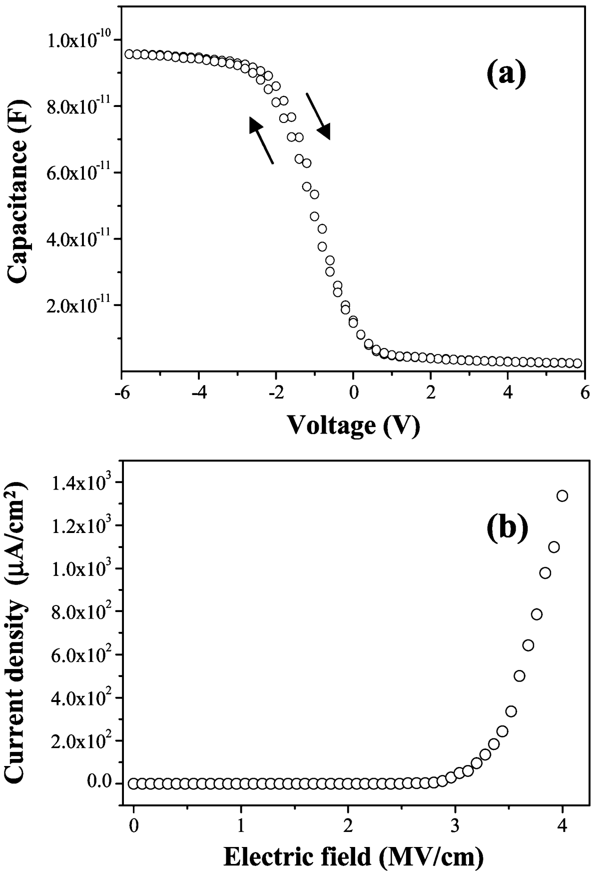
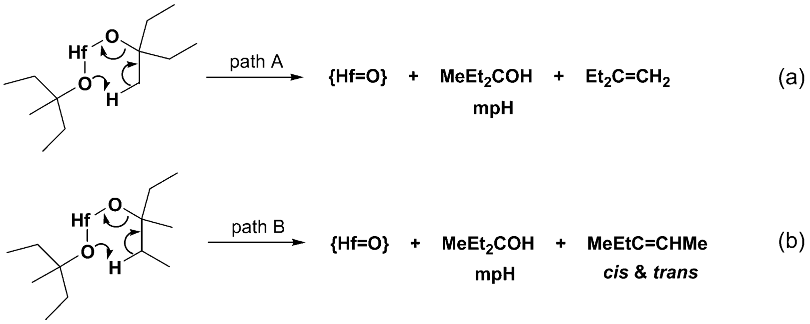


Figure 8. C−V curve (a) and I−V curve (b) of the Al/HfO_2 (24 nm)/p-type Si(001) structure with the HfO_2 film deposited at 400 °C.

Figure 6 shows the XP survey spectrum of an 80-nm-thick HfO_2 film deposited at 400 °C. In the spectrum, the photoelectron peaks of Hf 4p, Hf 4d, Hf 4f, and O 1s orbitals and the X-ray excited O KLL Auger peaks are easily recognizable. The Hf:O ratio calculated from the normalized peak areas of Hf 4d and O 1s orbitals is 1.0:2.1, which indicates that the film is stoichiometric in the surface region. Besides these relevant peaks there appear no other peaks signifying incorporation of impurity elements in the film. Especially, the C 1s region around 285 eV does not show any noticeable peak (after 5 min of Ar ion sputtering), which indicates that carbon incorporation is not above the detection limit of the XPS technique. The absence of carbon incorporation in the film was also confirmed by Auger depth profile analysis (Figure 7).

Scheme 1. Mechanism of Thermal Decomposition of Hafnium 3-Methyl-3-pentoxide {$Hf[OC(CH_3)(C_2H_5)_2]_4$, $Hf(mp)_4$}[a]



[a] Key: (a) β-Hydrogen elimination of the methyl group on the α-carbon. (b) β-Hydrogen elimination of the CH_2 group in the ethyl group.

Figure 7 shows the AES depth profile of the 80-nm-thick HfO_2 film. The Hf:O ratio is 1.0:1.85 in the bulk of the film, which is consistent with the expected stoichiometry due to the β-hydrogen elimination processes, explained later, of the $Hf(mp)_4$ single precursor. In particular, the carbon impurity level of the HfO_2 film is negligibly low, below 2%. As mentioned above, from the stoichiometry of the HfO_2 film and the negligible carbon incorporation shown in Figure 6, it is believed that the β-hydrogen elimination processes of the $Hf(mp)_4$ precursor were fully operational in the deposition of HfO_2 films with virtually no other additional decomposition and/or readsorption processes of the byproducts.

Figure 8a shows the C−V plot of an Al/HfO_2/p-type Si(100) metal insulator semiconductor (MIS) structure (measured at the frequency of 1 MHz) for which the 25-nm-thick HfO_2 film was deposited at 400 °C. The C−V curve demonstrated a clockwise hysteresis when swept from a positive to negative bias forward and from a negative to positive bias backward. The hysteresis width was about 0.2 V. This very low value of hysteresis is due to low concentrations of impurities (such as H^+) and low defect contents in our HfO_2 film. Also, the flat-band voltage shift of the C−V curve was −1.05 V. The flat-band voltage shift for an ideal capacitor with an Al electrode and a p-type Si substrate should be around −0.9 to −1.0 V.[30] The effective dielectric constant of the HfO_2 film was found to be 11.8 without annealing. The I−V characteristic for the same HfO_2 film is shown in Figure 8b, and the leakage current density was 2.43×10^{-7} A/cm^2. No breakdown was observed up to the applied voltage of ∼7 V. The results of the electrical measurements are comparable to those reported previously by CVD and ALD.[16,24]

Decomposition Mechanism of the Precursor. β-Hydrogen elimination has been successfully employed in the single-source CVD of simple oxides such as ZnO and MgO and complex oxides such as $MgAl_2O_4$. For instance, using the concept of β-hydrogen elimination, Auld et al.[31] reported the growth of ZnO films from methylzinc isopropoxide and methylzinc *tert*-butoxide as single-source precursors, in the absence of an added oxygen source. For MgO, the single precursor methylmagnesium *tert*-butoxide[32] was employed. The heterometallic single precursors $Mg[(\mu\text{-}O^iPr)_2AlMe_2]_2$[33] and $Mg[(O^tBu)_2AlH_2]_2$[34] were used to deposit $MgAl_2O_4$ thin films. Bradley et al.[35] studied the kinetics of the thermal decomposition of zirconium tetra-*tert*-amyloxide and elucidated the mechanism involving the hydrolysis of zirconium *tert*-alkoxide by water produced in the dehydration of the *tert*-alcohol. Nandi et al.[36] reported the mechanistic studies of pyrolytic transformation of homoleptic titanium alkoxides to titanium dioxide. The titanium complexes of tertiary alkoxides were decomposed to yield TiO_2, alcohols, and olefins, with no significant secondary reactions such as dehydration of alcohols. Recently, Bhakta et al.[37] disclosed the molecular mechanism in the decomposition of $[Ti(O^iPr)_2(tbaoac)_2]$ (tbaoac = *tert*-butylacetoacetato) by the formation of ketene intermediates. In this study, to investigate the decomposition mechanism of the $Hf(mp)_4$ single precursor in the MOCVD growth of HfO_2 films, the vapor phase reaction products, collected during the thermal decomposition at 400 °C, were analyzed by GC/MS and ^1H NMR spectroscopy. The reaction products identified by their gas chromatograms were mpH, $C(CH_3)(CH_2CH_3)_2OH$, *cis*- and *trans*-3-methyl-2-pentene, $CH_3CH{=}C(CH_3)CH_2CH_3$, and 2-ethyl-1-butene, $(C_2H_5)_2C{=}CH_2$. The identities of the olefins were confirmed by comparison of their gas chromatograms with those of the same olefins that we purchased from Sigma-Aldrich. The mass spectra of mpH and 3-methyl-2-pentene perfectly matched the spectra available from NIST.[38] From this result, the thermal decomposition of $Hf(mp)_4$ can be described by β-hydrogen elimination reactions through favorable six-membered transition states as shown in Scheme 1. Since the MOCVD was performed under a dynamic vacuum (approximately 10^{-2} mmHg), the organic compounds produced in the decomposition of $Hf(mp)_4$ must have been removed quickly. Therefore, the dehydration reaction of mpH does not seem to have taken place. Our MOCVD study thus differs from Bradley and Faktor's work[35] that was carried out under a static vacuum, where the alcohol formed underwent dehydration to generate water, which then caused autocatalytic decomposition of the metal alkoxide. The

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scheme shows two different β-hydrogen elimination reactions: one is the elimination of a β-hydrogen from the central methyl group (a) and the other is the elimination of a β-hydrogen from a methylenic group (b). The (a) process produces mpH (3-methyl-3-pentanol) and $(C_2H_5)_2C{=}CH_2$ (2-ethyl-1-butene), and the (b) process produces mpH and $CH_3CH{=}C(CH_3)CH_2CH_3$ in two isomeric forms, namely, the *cis*- and *trans*-3-methyl-2-pentene. The β-hydrogen atoms are abstracted by adjacent mp groups, which then leave the substrate surface as mpH, 3-methyl-3-pentanol. These products were all identified as explained above. Therefore the β-hydrogen elimination pathways can yield carbon-free, stoichiometric HfO_2 films on the substrates. There were no appreciable side reactions occurring, according to the GC/MS analysis of the vapor phase reaction products.

Conclusions

The new precursor, hafnium 3-methyl-3-pentoxide $\{Hf[OC(CH_3)(C_2H_5)_2]_4$, $Hf(mp)_4\}$, has been synthesized and used as a single precursor for the deposition of high-quality HfO_2 thin films by MOCVD. $Hf(mp)_4$ is a liquid at room temperature, and it is much more thermally stable than and as volatile as the conventional, rather unstable, alkoxide precursor $Hf(O^tBu)_4$. It can be thermally decomposed to stoichiometric HfO_2 films with no additional oxygen source. The activation energy of deposition was 68.1 kJ/mol. The HfO_2 films deposited at low temperatures were amorphous, and those grown above 350 °C were found to be monoclinic. Electrical characteristics of the HfO_2 films were comparable to those of the films obtained using other precursors. Its reaction mechanism was also investigated and found to be dominantly the β-hydrogen elimination processes. These results indicate that $Hf(mp)_4$ is a promising single precursor of hafnium oxide films.

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