

**Electrical properties of ultrathin  $\text{HfO}_2$  films for replacement metal gate transistors, fabricated by atomic layer deposition using  $\text{Hf}(\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5))_4$  and  $\text{O}_3$**

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# Electrical properties of ultrathin $\text{HfO}_2$ films for replacement metal gate transistors, fabricated by atomic layer deposition using $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$ and $\text{O}_3$

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Ultrathin  $\text{HfO}_2$  gate dielectric was fabricated by atomic layer deposition (ALD) technology using tetrakis(ethylmethylamino)hafnium  $\{\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4\}$ , with  $\text{O}_3$  as an oxidant for use in replacement metal gate transistors. From secondary ion mass spectrometry analyses, the ALD process temperature was very important for the fabrication of high-quality  $\text{HfO}_2$  films. The dielectric constant with 275 °C deposition was higher than that at 200–250 °C. Furthermore, the  $V_{\text{FB}}$  with 200 °C deposition was about 0.1–0.15 V lower than that at 275 °C, due to formation of high residual impurity concentrations, such as carbon, in the  $\text{HfO}_2$  films. The leakage current densities in the 275 °C case were reduced by about five orders with respect to reference  $\text{SiO}_2$  films. From these results, it was judged that the ALD process temperature of 275 °C was suitable for the fabrication of ultrathin  $\text{HfO}_2$  gate dielectrics necessary to improve the leakage current characteristics. © 2005 American Institute of Physics. [DOI: 10.1063/1.2072827]

Conventional thermal silicon dioxide ( $\text{SiO}_2$ ) films have been used as gate dielectrics for standard complementary metal oxide semiconductor devices because of their superior properties, such as large energy band gap (8.9 eV), low leakage current, low interface state density, and low impurities in the  $\text{SiO}_2$  films. For the gate oxide thickness of less than 3.5 nm, the direct tunneling current increases 100 times for every 0.4–0.5 nm decrease of thickness.<sup>1,2</sup> This high gate leakage current would increase standby power consumption. In order to reduce the leakage current by direct tunneling, the high dielectric constant (high- $k$ ) materials allow for an increase in the physical thickness to maintain a low equivalent oxide thickness. Among many high- $k$  materials, Hf-based and its nitride films are good for low leakage current and high carrier mobility. Therefore, sputter and/or metalorganic chemical vapor deposition methods are currently used for the high- $k$  film formation.<sup>3–9</sup>

Atomic layer deposition (ALD) technology is desirable for the precise control of composition, film thickness, conformality, and uniformity among many high- $k$  film deposition techniques.<sup>10–15</sup> Hafnium-tetrachloride ( $\text{HfCl}_4$ ) and water ( $\text{H}_2\text{O}$ ) were widely used for ALD  $\text{HfO}_2$  film formations.<sup>10–12</sup> Recently, there were reports using Hf amide-type precursors, such as  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  for ALD of  $\text{HfO}_2$  or Hf-aluminate films to solve the problem of particle formation or residual chlorine with  $\text{HfCl}_4$  precursors.<sup>13–15</sup> Furthermore, ALD  $\text{HfO}_2$  films were deposited at low temperature (around 300 °C) using  $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$  precursor and  $\text{O}_3$  as the oxidant during ALD instead of  $\text{H}_2\text{O}$ , those films contained much smaller residual impurities such as carbon or nitrogen from previous precursors.<sup>14</sup> The melting point of the  $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$  precursor is about 28 °C. At that temperature, it is difficult to use the conventional liquid supply system because it has a condensation problem of the liquid supply lines under the room temperature. On the other hand, the  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  precursor is a good material because the

melting point is very low (less than –70 °C) to maintain the middle vapor pressure (4.8 Torr at 120 °C).<sup>15</sup> However, there were few papers about the relationship between the residual impurities and the electrical properties for  $\text{HfO}_2$  gate dielectrics using  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  and  $\text{O}_3$ . Furthermore, metal gate and high- $k$  dielectric transistors can be fabricated by using the damascene gate process<sup>16</sup> and the replacement gate process.<sup>17</sup> In these processes, the salicide films, such as NiSi or CoSi, are required on source/drain regions in order to obtain the lowering of contact resistance and the increased performance of the  $I_{\text{on}}\text{--}I_{\text{off}}$  characteristics.<sup>18,19</sup> Thus, the process temperature after the salicide film formation can be lowered to below 600 °C to maintain the good characteristics of metal/high- $k$  gate transistors.

We investigated  $\text{HfO}_2$  gate dielectrics using  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  and  $\text{O}_3$  as replacement metal gate transistors. In this study, the residual impurities and the electrical properties, of  $\text{HfO}_2$  gate dielectrics formed using different ALD process temperatures, were compared.

Substrates were 12 in.  $p$ -type Si (100) wafers. Right after a diluted (0.5%) HF treatment,  $\text{HfO}_2$  films were directly deposited with a single-type ALD equipment using  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  precursor. A single ALD cycle for  $\text{HfO}_2$  consisted of the following process.  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  precursor was introduced to the reactor chamber for 20 s, and this was then purged for 30 s. This precursor was introduced using a liquid flow meter system, and that vaporized at 120 °C with Ar as a carrier gas. The  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  and carrier gas have flow rates of 75 mg/min and 300 standard cubic centimeter/min (sccm), respectively. Following this, an oxidant  $\text{O}_3$  was introduced for 5 s, and purged for 30 s. The buffer Ar gas was always flowing at 700 sccm in the reactor chamber.  $\text{O}_3$  was used as a source of oxygen using a  $\text{O}_2/\text{N}_2$  flow ratio of 1 standard liter/min/0.1 sccm with the concentration of  $\text{O}_3$  in  $\text{O}_2$  being 100 g/Normal cubic meter ( $\text{Nm}^3$ ). The pressure in the reactor chamber was controlled by an autoperessure control.  $\text{HfO}_2$  films were deposited at temperatures ranging

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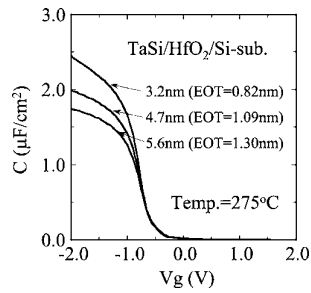


FIG. 1.  $C$ - $V$  characteristics on  $\text{HfO}_2$  film thickness with gate electrodes of  $\text{TaSi}_{2.5}$ (10 nm)/ $\text{W}$ (100 nm).  $C$ - $V$  measurements were performed at high-frequency (100 kHz) using capacitors with an area of  $2.5 \times 10^{-5} \text{ cm}^2$ .  $\text{HfO}_2$  films were deposited at 275 °C and 0.5 Torr. The EOT and the ( $V_{\text{FB}}$ ) were calculated from the analytical quantum mechanical model (Ref. 21).

from 200 °C to 300 °C and the pressure was kept at 0.5 Torr. The thickness and uniformity of the  $\text{HfO}_2$  films were measured with an ellipsometer over 12 in. wafers. The impurities, such as carbon, hydrogen, and nitrogen of the  $\text{HfO}_2$  gate dielectrics, were investigated by secondary ion mass spectrometry (SIMS) analysis with a 1 keV cesium primary ion ( $\text{Cs}^+$ ) beam. The primary ion beam was raster scanned over an area of  $350 \times 350 \mu\text{m}^2$ .

After  $\text{HfO}_2$  film deposition, the films were annealed in an  $\text{O}_3$  ambient at 5.0 Torr and at 275 °C for 60 s with the concentration of  $\text{O}_3$  in  $\text{O}_2$  being 100 g/ $\text{Nm}^3$ . Capacitors were formed using sputter- $\text{TaSi}_{2.5}$  (10 nm)/ $\text{W}$ (100 nm) gate electrodes, followed by photolithography and dry etching steps to pattern the electrodes.  $\text{TaSi}_{2.5}$  gate electrodes were used for flat-band voltage ( $V_{\text{FB}}$ ) control of  $n$ -metal-oxide-semiconductor field effect transistors (MOSFETs).<sup>20</sup> Those capacitors were annealed at 400 °C for 30 min in the forming gas ( $\text{N}_2/\text{H}_2$  mixture). The capacitance-voltage ( $C$ - $V$ ) and current-voltage ( $I$ - $V$ ) measurements were performed in parallel mode on an HP 4284A LCR meter at high frequency (100 kHz) and an HP 4156C parameter analyzer. The effective oxide thickness (EOT) and ( $V_{\text{FB}}$ ) were calculated from the analytical quantum mechanical model.<sup>21</sup>

Figure 1 indicates the dependence of  $C$ - $V$  curves on the  $\text{HfO}_2$  film thickness with gate electrodes of  $\text{TaSi}_{2.5}$ (10 nm)/ $\text{W}$ (100 nm).  $C$ - $V$  measurements were performed at high-frequency (100 kHz) using capacitors with an area of  $2.5 \times 10^{-5} \text{ cm}^2$ .  $\text{HfO}_2$  films were deposited at 275 °C and 0.5 Torr. As shown in Fig. 1, EOT were 0.82 nm, 1.09

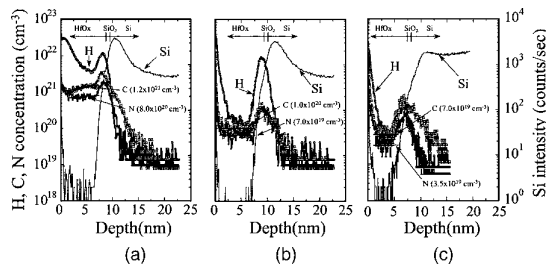


FIG. 2. SIMS depth profiles of ALD  $\text{HfO}_2$  films. The film depositions were carried out at: 200 °C (a), 250 °C (b), and 275 °C (c), respectively. The pressure in the reactor chamber was kept at 0.5 Torr. SIMS analyses were measured with a 1 keV cesium primary ion ( $\text{Cs}^+$ ) beam. On the left-hand side of the vertical axis, carbon, hydrogen, and nitrogen impurities are indicated as the concentrations ( $\text{cm}^{-3}$ ). On the right-hand side of the vertical axis, Si atoms are indicated as secondary ion intensities (counts/s).

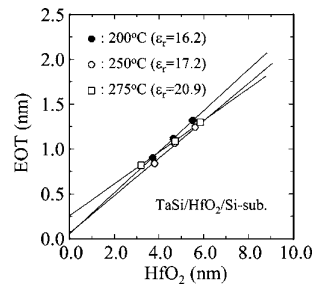


FIG. 3. Dependence of EOT on the  $\text{HfO}_2$  film thickness at different ALD process temperatures with gate electrodes of  $\text{TaSi}_{2.5}$ (10 nm)/ $\text{W}$ (100 nm).

nm, and 1.30 nm for 3.2 nm, 4.7 nm, and 5.6 nm  $\text{HfO}_2$  film thickness, respectively. This showed that ultrathin EOT films of about 0.8 nm could be fabricated using thin  $\text{HfO}_2$  gate dielectrics and  $\text{TaSi}_{2.5}$  gate electrodes. Furthermore,  $V_{\text{FB}}$  values obtained of about  $-0.67 \text{ V}$  were suitable for  $n$ -MOSFETs.

Figure 2 shows the SIMS depth profiles of ALD  $\text{HfO}_2$  films. As shown in Figs. 2(a)–2(c), the ALD process temperatures used were 200 °C, 250 °C, and 275 °C, respectively. The pressure in the reactor chamber was kept at 0.5 Torr. SIMS analyses were measured with a 1 keV cesium primary ion ( $\text{Cs}^+$ ) beam. On the left-hand side of the vertical axis, carbon, hydrogen, and nitrogen impurities are indicated as the concentrations ( $\text{cm}^{-3}$ ). On the right-hand side of the vertical axis, Si atoms are indicated as secondary ion intensities (counts/s). As shown in Fig. 2(a), the average impurity concentrations of carbon ( $1.2 \times 10^{21} \text{ cm}^{-3}$ ) and nitrogen ( $8 \times 10^{20} \text{ cm}^{-3}$ ) were at a high level in the ALD  $\text{HfO}_2$  films, because the ALD process temperature of 200 °C was too low. By increasing the ALD process temperature to 250 °C, the average impurity concentrations of carbon ( $1 \times 10^{20} \text{ cm}^{-3}$ ) and nitrogen ( $7 \times 10^{19} \text{ cm}^{-3}$ ) were remarkably reduced [Fig. 2(b)]. The impurity concentrations of carbon ( $7 \times 10^{19} \text{ cm}^{-3}$ ) and nitrogen ( $3.5 \times 10^{19} \text{ cm}^{-3}$ ) were further reduced by using an ALD process temperature of 275 °C [Fig. 2(c)]. The high level of impurities in the  $\text{HfO}_2$  films at low ALD process temperatures, around 200 °C, resulted from the desorption of carbon or nitrogen using a  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  precursor not being sufficiently removed by  $\text{O}_3$  oxidant. A thickness uniformity of less than 5% could be obtained at 200–275 °C. The thickness uniformity was calculated from the following equation: Uniformity = (maximum thickness – minimum thickness)/(average thickness  $\times$  2) using 49 data points over a 12 in.

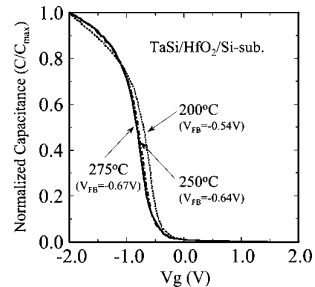


FIG. 4. Dependence of the normalized capacitance curves on  $\text{HfO}_2$  film process temperatures with gate electrodes of  $\text{TaSi}_{2.5}$ (10 nm)/ $\text{W}$ (100 nm).  $V_{\text{FB}}$  were calculated from the analytical quantum mechanical model (Ref. 21).

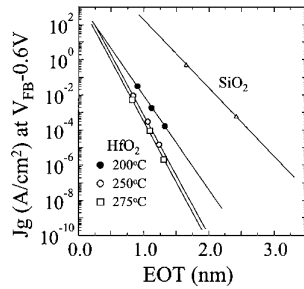


FIG. 5. Leakage current density at  $V_{FB}=0.6$  V as a function of EOT for  $n$ -MOSFETs.  $I$ - $V$  measurements were performed using capacitors with an area of  $2.5 \times 10^{-5}$  cm<sup>2</sup>.

wafer. However, this was remarkably increased to above 15% at 300 °C. Thus, the most suitable ALD process temperature is about 275 °C for the fabrication of high-quality  $\text{HfO}_2$  films in this ALD process equipment.

Figure 3 shows the dependence of EOT on the  $\text{HfO}_2$  film thickness at different ALD process temperatures, using  $\text{TaSi}_{2.5}$ (10 nm)/W(100 nm) gate electrodes. As shown in Fig. 3, EOT was linearly dependent on the physical  $\text{HfO}_2$  film thickness. However, the slope was different for each process temperature. From these results, the dielectric constants ( $\epsilon_r$ ) were about 16.2, 17.2, and 20.9 for 200 °C, 250 °C, and 275 °C ALD process temperatures, respectively. It is considered that the dielectric constant for 275 °C is higher than that for 200–250 °C, due to the fabrication of high-quality  $\text{HfO}_2$  films. Furthermore, the plots show EOT values of about 0.01 nm and 0.025 nm at zero-film thickness for 200–250 °C and 275 °C depositions, respectively. This is suggested that the 0.025 nm for 275 °C results from higher oxidation than that seen at 200–250 °C in an  $\text{O}_3$  oxidant, because of the higher temperature used for the ALD oxidation process.

Figure 4 shows the dependence of the normalized capacitance curves on the  $\text{HfO}_2$  film process temperatures with  $\text{TaSi}_{2.5}$ (10 nm)/W(100 nm) gate electrodes.  $V_{FB}$  values were calculated from the analytical quantum mechanical model.<sup>21</sup> As shown in Fig. 4,  $V_{FB}$  values obtained were  $-0.54$  V,  $-0.64$  V, and  $-0.67$  V for 200 °C, 250 °C, and 275 °C ALD process temperatures, respectively. It is considered that the  $V_{FB}$  for the 200 °C process is about 0.1–0.15 V higher than that for 275 °C, due to formation of high residual impurity concentrations, such as carbon in the  $\text{HfO}_2$  films.

Figure 5 shows the leakage current density at  $V_{FB}=0.6$  V as a function of EOT for  $n$ -MOSFETs. The leakage current densities for 200 °C  $\text{HfO}_2$  gate dielectrics are reduced by about four orders of the magnitude with respect to reference  $\text{SiO}_2$  films. Furthermore, the values for 275 °C processing are reduced by about one order with respect to the 200 °C sample. From these results, the ALD process temperature at 275 °C is most suitable for the fabrication of ultrathin  $\text{HfO}_2$  gate dielectrics to improve leakage current characteristics.

We studied ultrathin  $\text{HfO}_2$  gate dielectrics of about 0.8 nm, formed by ALD technology using the  $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$  and  $\text{O}_3$  as oxidant, for the replacement metal gate transistors. This precursor was a good material, because its melting point was very low (less than  $-70$  °C), to maintain an average vapor pressure of 4.8 Torr at 120 °C. From SIMS analyses, the ALD process temperature was very important for the fabrication of high-quality  $\text{HfO}_2$  films, in as much as,

at 275 °C, the concentration of residual impurities, such as carbon and nitrogen, were remarkably reduced. The dielectric constant for 275 °C films was higher than for 200–250 °C because of the high quality of the fabricated  $\text{HfO}_2$  films. Furthermore, the  $V_{FB}$  with the 200 °C films was about 0.1–0.15 V lower than that with 275 °C films, due to formation of high concentrations of residual impurities, such as carbon in the  $\text{HfO}_2$  films. The leakage current densities for 275 °C films were reduced by about five orders of magnitude with respect to reference  $\text{SiO}_2$  films. These results indicated that an ALD process temperature of 275 °C was suitable for the fabrication of ultrathin  $\text{HfO}_2$  gate dielectrics to gain improvement in the leakage current characteristics.

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