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Comparison of HfO_2 films grown by atomic layer deposition using $HfCl_4$ and H_2O or O_3 as the oxidant

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HfO_2 gate dielectric thin-films were deposited on Si wafers using an atomic-layer deposition (ALD) technique with $HfCl_4$ and either H_2O or O_3 as the precursor and oxidant, respectively. Although the ALD reactions using either H_2O or O_3 were successfully confirmed at a deposition temperature of 300 °C, the structural and electrical properties of the HfO_2 films grown using the two oxidants were quite different. The stronger oxidation power of the O_3 compared to H_2O increased the oxygen concentration in the HfO_2 film and the rate of interfacial SiO_2 formation even at the as-deposited state. Because of the larger oxygen concentration, the decrease in the capacitance density of the film grown with O_3 after rapid thermal annealing at 750 °C under N_2 atmosphere was slightly larger than that of the HfO_2 film grown with H_2O. Apart from this weakness, all the other electrical properties, including the fixed charge density, the interface trap density, the leakage current density and the hysteresis in the capacitance–voltage plot of the film grown with O_3 were superior to those of the film grown with H_2O. Therefore, O_3 appears to be a better oxidant for the HfO_2 film growth using the ALD method. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1599980]

I. INTRODUCTION

As complementary metal–oxide–semiconductor field effect transistor (CMOSFET) device scaling reaches the sub-0.1 μm era, high dielectric (high-k) HfO_2 thin films are attracting increasing interest as a replacement for nitrided SiO_2 gate oxide films.[1–4] Physically thicker high-k HfO_2 films can greatly suppress the gate leakage current (I_{gate}) while maintaining a high gate capacitance. A high gate capacitance is essential in order to minimize the short-channel effect and to maximize the drain saturation current as well as to achieve the channel controllability of the gate.

The atomic layer deposition (ALD) process appears to be one of the most suitable methods for the high-k film growth due to its excellent process controllability even for extremely low thickness (<5 nm) high-k films.[5,6] However, most vapor-phase grown HfO_2 thin films appear to have interfacial layers (ILs) at the Si interface due to the presence of excess oxidizing elements, and simultaneous Si diffusion into the growing films.[7,8] This reduces the overall capacitance density, which needs to be minimized in order to realize the high-k characteristics. The other serious drawback of high-k gate oxides compared to SiO_2 is the high interfacial fixed-charge density (Q_f)[9,10] and the high interface trap density (D_{it}).[2,11] The high Q_f and D_{it} adversely affect the device operation of the CMOSFET.

The commonly used precursor and oxidant for ALD of HfO_2 films are the $HfCl_4$ and H_2O, respectively. This is because of the existence of a proper ligand exchange reaction between the two materials, which is inevitable for an ALD reaction to occur at a relatively low temperature (200–400 °C)[8] without thermal decomposition of the precursors. However, the HfO_2 films grown from the $HfCl_4$ contain a rather high concentration of Cl,[12] which might adversely affect the thermal stability and electrical performances of the film used as a gate dielectric. Lysaght *et al.*[13] recently reported that residual Cl ions in ALD HfO_2 films grown using $HfCl_4$ and H_2O attack the underlying Si substrate and made voids in Si during postannealing, which is fatal to the MOSFET fabrication and operation. There might be some residual OH^- and H^+ ions cracked from H_2O in the film, which can also degrade the film properties.

O_3 has been used to grow high quality Al_2O_3 films by the ALD using the $Al(CH_3)_3$ as the Al precursor.[14,15] Compared to the Al_2O_3 films grown by ALD using H_2O as the oxidant, the films grown using O_3 appeared to have less incompletely oxidized Al ions,[14] thereby showing a better electrical performance, such as a smaller leakage current at a similar equivalent oxide thickness (EOT).[15] This can be attributed to the higher oxidizing power of O_3 compared to that of the H_2O. Therefore, this study used O_3, for the first time, for the ALD of HfO_2 films using the $HfCl_4$ precursor, and the growth behavior and structural and electrical proper-

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ties of the films were compared to those of the films grown with the H_2O oxidant.

II. EXPERIMENTAL PROCEDURE

15–17-nm-thick HfO_2 films were grown by an ALD process using $HfCl_4$ and H_2O or O_3 as the precursor and oxidant, respectively, at a wafer temperature of 300 °C on B-doped *p*-type 8-in.-diam (100) Si wafers (doping concentration of $1\times10^{15}\,cm^{-3}$). The native oxide on the Si wafer surface was removed by RCA cleaning immediately prior to HfO_2 film growth. Here, the film thickness was far larger than that used for the practical applications (3–4 nm). There are several reasons for such a large thickness. First was to measure the D_{it} using the conductance method, which requires a very low leakage current density ($\sim10^{-8}\,A\,cm^{-2}$). It has been reported that single layer HfO_2 films with an EOT of 1–2 nm show a relatively large leakage (10^{-3}–$10^{-1}\,A\,cm^{-2}$) in the voltage region of interest, which renders the application of conductance method impossible.[16] The thick film in this study suppresses the leakage current to sufficiently low levels in the voltage region of interest so that the D_{it} could be successfully measured using the conductance method. Second, the qualitative analysis of the structural variation of the film, such as x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) with the variation in the oxidants required a rather thick film. It has been reported that ALD HfO_2 films remain amorphous when the film thickness is small ($<\sim5$ nm) irrespective of the deposition conditions.[8] The rather thick films in this study were crystallized even at the as-deposited state. Therefore, a comparison between the crystallization behaviors of the HfO_2 films grown with either the H_2O or O_3 becomes feasible.

Postannealing of the samples was performed using a rapid thermal annealing (RTA) process at temperatures ranging from 700 to 900 °C for 60 s in a pure N_2 atmosphere.

The film thickness and crystalline structures were investigated by ellipsometry, HRTEM, and XRD. Ten HRTEM pictures were taken for each sample to compensate for the error in the film thickness measurements due to local variations. The chemical composition and binding status of the films were investigated by secondary-ion mass spectroscopy (SIMS) and x-ray photoelectron spectroscopy (XPS) using Mg $K\alpha$ radiation with a photon energy 1253.6 eV. The overall energy resolution was approximately 1 eV. For XPS analysis, 2–3-nm-thick HfO_2 films were grown with the H_2O and O_3 oxidants, respectively.

The metal–insulator–semiconductor capacitors (MIS-CAPs) were fabricated by depositing Pt top electrodes using an electron beam evaporation method through a shadow mask. The accurate electrode area of each measured capacitor was measured by optical microscopy. The backside of the wafer was HF cleaned with Al metallization being subsequently applied. The MIS CAP was annealed at 400 °C for 30 min under a 5% H_2/95% N_2 atmosphere. A Hewlett–Packard 4194A impedance meter and a 4140B picoammeter were used for the capacitance–voltage (C–V) and the current density–voltage (J–V) measurements, respectively.

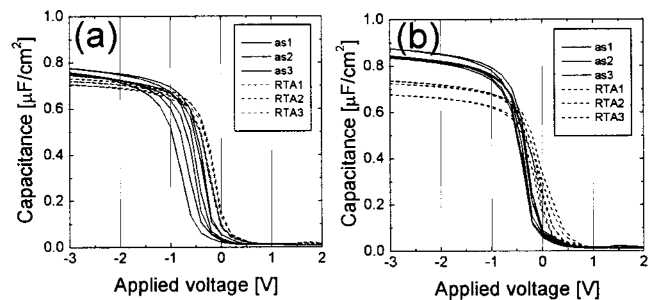

FIG. 1. C–V curves of the MIS capacitor at the as-deposited state and after RTA at 750 °C of the HfO_2 film with (a) H_2O and (b) O_3 as oxidants.

Five to ten capacitors were measured from each sample to compensate for local variations. The C–V measurement frequency was 1 MHz. The conductance method was adopted to estimate the D_{it}.[16] Capacitance equivalent thickness (CET), flatband voltage shift (V_{fb}), and hysteresis voltage (V_{hy}) were extracted from the high-frequency C–V curves.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the C–V curves of the MIS CAPs at the as-deposited state and after RTA at 750 °C of the HfO_2 film with the H_2O and O_3 oxidants, respectively. The C–V curves show a good saturation behavior due to the low leakage current, as shown in Fig. 2. Therefore, the CET was calculated from the accumulation capacitance (at −3 V). The variations in the CET values of the two HfO_2 films before and after postannealing are summarized in Table I along with the other electrical parameters as well as the thickness of each layer. First, the CET of the as-deposited HfO_2 film grown with O_3 shows a smaller CET by 0.5 nm than that of the film grown with H_2O, which was due to the smaller thickness of the film as shown by the HRTEM in Fig. 4. However, the CETs of the films after RTA at 750 °C were almost the same indicating an inferior thermal stability of the HfO_2 film grown with the O_3 oxidant. This was attributed to the higher oxygen concentration of the film grown with the O_3 oxidant, as will be discussed later. Therefore, a fair comparison can be made by comparing the other electrical properties, such as the J, V_{fb}, V_{hy}, and D_{it}, of the two films after RTA.

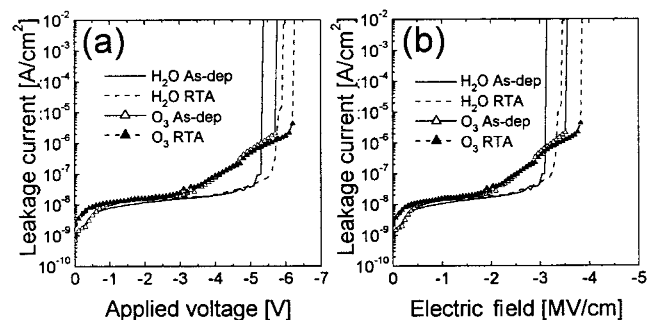

FIG. 2. (a) J–V and (b) J–E curves of the MIS capacitor at the as-deposited state and after RTA at 750 °C of the HfO_2 film grown with H_2O and O_3 as oxidants.

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TABLE I. Summary of the electrical results and the thickness variations.

Type of oxidant	Status	CET (nm) (−3 V)	Leakage (A/cm^2) (−1 V)	Hysteresis in $C-V$ (mV)	Flatband voltage (mV)	Interlayer thickness (nm)	Upper-layer thickness (nm)	Total layer thickness (nm)
H_2O	As-deposited	4.53	1.1×10^{-8}	161	−890	1.6	15.5	17.1
	RTA	4.80	1.4×10^{-8}	81	−520	1.4	15.8	17.2
O_3	As-deposited	4.05	9.1×10^{-9}	92	−630	1.4	14.8	16.2
	RTA	4.85	1.0×10^{-8}	36	−300	1.7	14.5	16.2

The V_{fb} due to the fixed charges, which are assumed to be located at the interfacial layer/HfO_2 interface, were calculated by subtracting 0.6 V from the measured flatband voltage shift in the high frequency $C-V$ curves in Fig. 1. Here the 0.6 V was the difference between the gate Pt work function [~5.6 eV for the (111) oriented Pt film] and Fermi level of the substrate Si. Figure 1 and Table I show that the HfO_2 film grown with O_3 has a smaller V_{fb} both at the as-deposited state and after RTA compared to that of the film grown with H_2O at each state. The negative signs of all the measured V_{fb} values show that there are positive fixed charges irrespective of the type of oxidant used. The positive sign of the fixed charges at the HfO_2/Si or HfO_2/SiO_2 interfaces coincides very well with the theoretical estimation based on the bonding structure of the HfO_2[17] and recent experimental observations.[18] The smallest fixed charge density (Q_f) observed for the case of the HfO_2 film grown with O_3 after RTA was still quite high ($\sim 2.2\times10^{12}\,cm^{-2}$) compared to the SiO_2/Si interface. Here, the Q_f was calculated by multiplying the V_{fb} by capacitance density of the HfO_2 films. The capacitance densities of the HfO_2 films were calculated using the CET of HfO_2 layer, which was estimated by subtracting the interfacial layer CET from the measured CET. The interfacial layer CET was estimated from its physical thickness, observed by HRTEM, and the dielectric constants, which were assumed to be 6–7 and 4 for the as-deposited state and after RTA, respectively. Therefore, it is necessary to use a certain method to compensate for the positive fixed charge, such as adopting a thin Al_2O_3 layer[19] or incorporating nitrogen into the high-*k* film or interfacial layer for their practical application to MOSFET.[20]

The smaller V_{hy} measured from the voltage sweep from accumulation to inversion and back to accumulation shows that the HfO_2 film with the O_3 has a smaller density of slow interface states than that of the film grown with the H_2O. The acceptable V_{hy} level (<50 mV) was obtained only from the HfO_2 film grown with O_3 after RTA. It should be noted that the thicker high-*k* films usually show a larger V_{hy} due to the larger total number of slow state centers. Therefore, the V_{hy} of 36 mV is a very promising value considering the large thickness of the current single-layer HfO_2 film.

Figures 2(a) and 2(b) show $J-V$ and $J-E$ curves, respectively, of the MIS capacitor at the as-deposited state and after RTA at 750 °C of the HfO_2 film with the H_2O and O_3 oxidants. Here, the electric field (E) was the apparent electric field calculated by simply dividing the applied voltage by the total film thickness measured by HRTEM. The leakage current densities in the low voltage region (<-3 V) were very low ($<-5\times10^{-8}\,A/cm^{-2}$), irrespective of the types of the oxidants and postannealing due to the thick thickness of the films. However, the J in the high voltage (>-3 V) region before breakdown was larger for the case of the films grown with O_3. Interestingly, RTA does not change at all the J values irrespective of the types of the oxidants used but increases the breakdown field (E_{bd}). The E_{bd} of the HfO_2 films with O_3 were larger than those of the films using H_2O. The higher E_{bd}s of the as-deposited films and after RTA with the O_3 oxidant are believed to be due to the smaller surface roughness of the films as shown by atomic force microscopy (AFM) in Fig. 3. The rms roughness of the HfO_2 films grown with the H_2O is 2–3 times larger than that of the films grown with the O_3 oxidant. The higher E_{bd} of the film after RTA with the O_3 oxidant compared to that of the as-deposited film is believed to be due to the larger interfacial layer thickness, which must have a higher resistivity, although the surface roughness slightly increased.

The fast increasing J after approximately −3 V prior to the breakdown of the film grown with O_3 might be related to the tunneling behavior due to the smaller thickness. Detailed analysis results for the leakage current mechanism of both samples will be reported in a later publication.

Figures 4(a)–4(d) show the HRTEM pictures of the as-deposited and RTA samples grown with the H_2O and O_3 oxidants, respectively. The films appear to have partially crystallized structures at the as-deposited state and have better crystalline qualities after RTA. Although the comparison of the degree of crystallization of the samples using the HRTEM is not quantitative, the as-deposited film with the H_2O

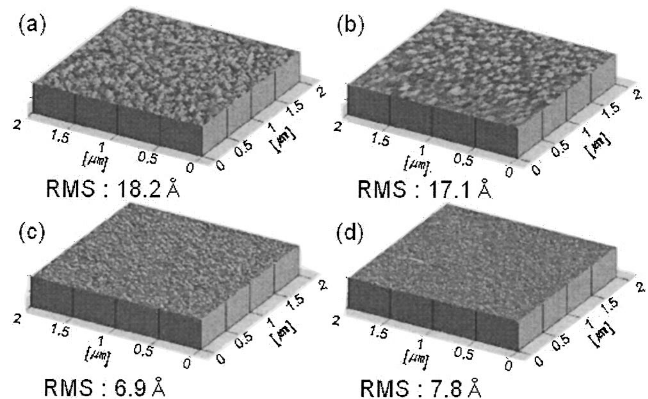

FIG. 3. AFM images of the (a) as-deposited sample grown with H_2O, (b) RTA sample grown with H_2O, (c) as-deposited sample grown with O_3, and (d) RTA sample grown with O_3.

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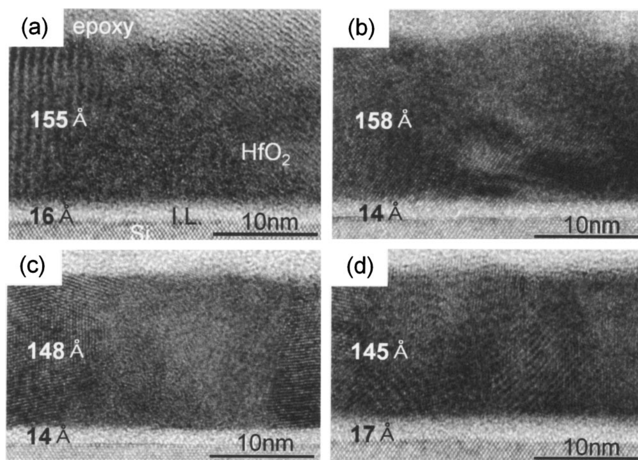

FIG. 4. HRTEM pictures of the (a) as-deposited sample grown with H_2O, (b) RTA sample grown with H_2O, (c) as-deposited sample grown with O_3, and (d) RTA sample grown with O_3.

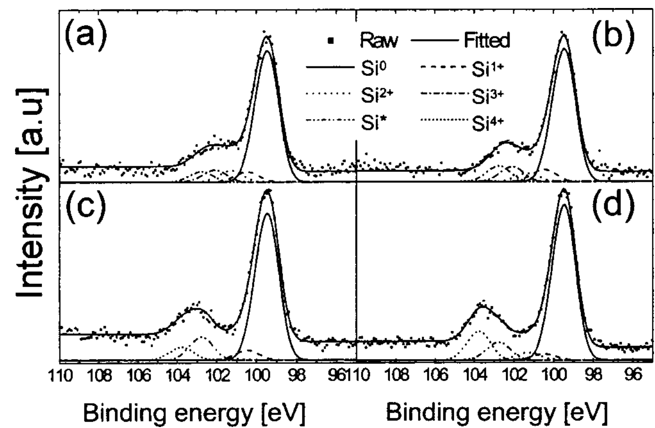

FIG. 6. Si $2p$ XPS spectra of the (a) as-deposited sample grown with H_2O, (b) RTA sample grown with H_2O, (c) as-deposited sample grown with O_3, and (d) RTA sample grown with O_3.

oxidant appeared to have a relatively poor crystalline quality from the extensive HRTEM observations (more than ten HRTEM images). A more quantitative comparison between the crystalline qualities of the films was made using the XRD, as shown in Fig. 5. The films are composed of a thick HfO_2 layer and thin interfacial layer. The thicknesses of each layer are included in Table I, where the thicknesses are the averaged values from ten HRTEM pictures of each sample. It has been reported that the thin HfO_2 films ($<\sim 5$ nm) grown directly on Si wafer at temperatures between 200 and 400 °C using the ALD method usually contain a rather high concentration of Si forming a Hf-rich Hf silicate.[8] The ILs contain some amount of Hf, particularly at the as-deposited state, forming a Si-rich Hf silicate.[7] However, the films in this study are rather thick and the surface regions (at least down to 10 nm depth from the surface) are almost completely free from Si impurities, as shown by the SIMS in Fig. 7. The IL thickness of the film grown with H_2O slightly decreases (by ~0.2 nm) whereas that of the film grown with O_3 slightly increases (by ~0.3 nm) after RTA. This increase in the IL thickness is due to oxidation of the Si substrate by the excess oxygen that was contained in the HfO_2 film itself, and not by oxygen diffusion from the atmosphere. This can be confirmed by the XPS and SIMS results shown in Figs. 6 and 7, respectively.

Figure 5 shows the θ–2θ XRD results of the samples before and after RTA at 750 °C. The as-grown film with the H_2O oxidant shows small peaks corresponding to crystalline $HfSiO_4$ with no peaks corresponding to the HfO_2, although HRTEM showed the crystalline lattice fringes, which might be due to the small crystallite size of the HfO_2 film. The presence of the $HfSiO_4$ phase corresponds to the Si diffusion into the HfO_2 film shown in the SIMS profile (Fig. 7). After RTA, peaks corresponding to the monoclinic HfO_2 appear, suggesting the improvement in the crystalline quality or grain growth of the HfO_2, with a decrease in the intensity of the $HfSiO_4$ peak. The as-grown film with O_3 shows HfO_2

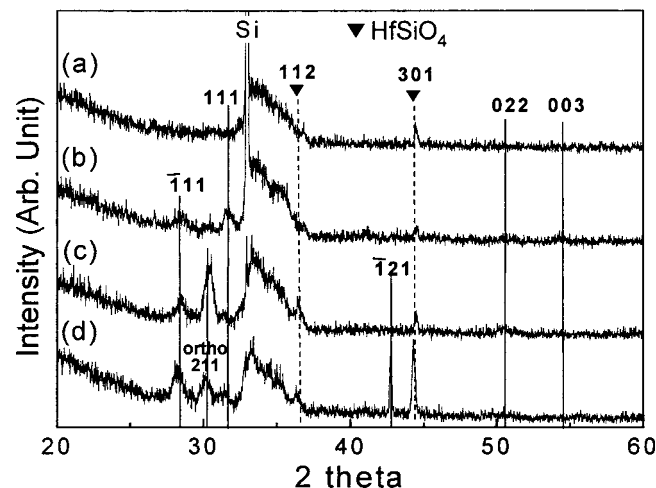

FIG. 5. XRD spectra of the (a) as-deposited sample grown with H_2O, (b) RTA sample grown with H_2O, (c) as-deposited sample grown with O_3, and (d) RTA sample grown with O_3.

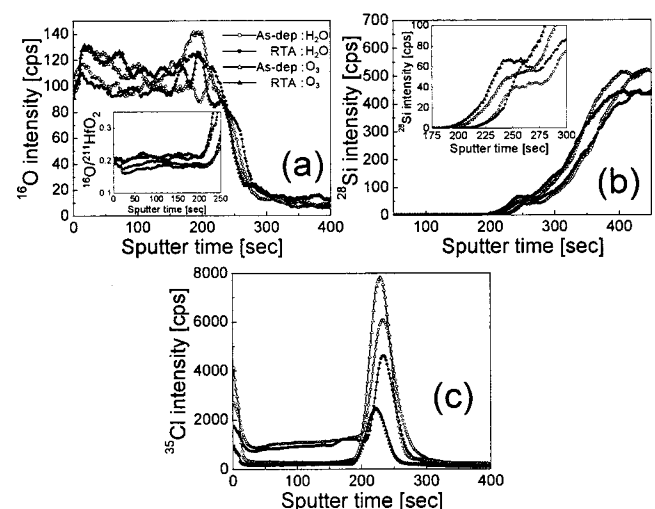

FIG. 7. SIMS depth profile results of (a) O (with mass 16) and (b) Si (with mass 28) of the thick HfO_2 films grown with the H_2O and O_3 before and after RTA at 750 °C. The inset (a) shows the variation in the O count/HfO_2 (with mass 211) count ratio. The inset (b) shows the variation in the Si count near interface in detail. (c) Cl concentration profiles of the four samples.

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peaks corresponding to the monoclinic and orthorhombic phases in addition to the $HfSiO_4$ peaks. This suggests that the films grown with O_3 are better crystallized compared to the films grown with H_2O although the growth temperatures were identical. Interestingly, RTA increases the $HfSiO_4$ peak intensity in this case, whereas the films grown with the H_2O showed a lower $HfSiO_4$ peak intensity after the same RTA, suggesting more Si-diffusion into the film occurred during RTA. This well corresponds to the Si concentration variation according to RTA estimated by the SIMS analysis shown in Fig. 7. RTA increased the Si concentration at the interface regions [see Fig. 7(b)]. RTA increases the monoclinic HfO_2 peak intensities whereas the peak intensity corresponding to the orthorhombic HfO_2 decreased. This is consistent with the fact that the monoclinic phase is the stable HfO_2 phase at these temperatures.

The variations in the chemical composition and binding status of the HfO_2 films with variations in the oxidants concentration (H_2O versus O_3) and RTA were investigated by XPS. Since the 15–17-nm-thick HfO_2 layer did not provide information on the interfaces, the HfO_2 layer thickness was reduced to 2–3 nm for the XPS analysis. To more clearly observe the thermal treatment effect and to be more practical for the device fabrication, RTA temperature was increased to 950 °C for these thin samples. Figure 6 shows the Si $2p$ XPS spectra of the: (a) as-deposited sample grown with H_2O, (b) postannealed sample grown with H_2O, (c) as-deposited sample grown with O_3, and (d) postannealed sample grown with O_3. The spectra were deconvoluted assuming the presence of Si^0 (Si substrate), Si^{1+}, Si^{2+}, Si^{3+}, Si* (Hf silicate), and Si^{4+} (SiO_2) ions. The Si substrate peak was fixed at 99.3 eV. The variations in the Si* and Si^{4+} peaks according to variation in the oxidant type during ALD and RTA should be noted. The as-deposited film grown with the O_3 shows a rather strong Si^{4+} peak suggesting SiO_2 formation at interface during film deposition. However, the as-deposited film grown with the H_2O shows no Si^{4+} peak suggesting that SiO_2 was not formed at the interface during film deposition. Therefore, the ILs that were observed in the HRTEM of Fig. 4, comprised of SiO_2, Si suboxides and Si-rich Hf silicate for the case of the sample grown with the O_3, and merely Si suboxides and Si-rich Hf silicate for the case of the sample grown with the H_2O. This might be due to the higher oxidation potential of the O_3 compared to that of the H_2O. It should be noted that there is almost no Si^{4+} signal detected for the case of the sample grown with the H_2O even after RTA. This clearly shows that there were barely any oxygen diffusion from the atmosphere and the formation of interfacial SiO_2 during RTA at this temperature (950 °C) and time duration (1 min). In contrast, there is a certain increase in the Si^{4+} peak intensity after RTA for the case of the film grown with O_3. This suggests that oxygen, which is responsible for the interfacial SiO_2 formation, was supplied from the HfO_2 film itself grown with the O_3. This is consistent with the increase in the IL thickness by RTA observed by HRTEM only for the case of O_3 in Fig. 4. The reason for the enhanced oxidation of the Si substrate during film growth and RTA can be found from the SIMS results.

Figures 7(a) and 7(b) shows the SIMS depth profile results of O (with mass 16) and Si (with mass 28), respectively, of the thick HfO_2 films grown with the H_2O and O_3 before and after RTA at 750 °C. The inset figure in (a) shows the variation in the O count/HfO_2 (with mass 211) count ratio, which was included to more clearly show the higher concentration of oxygen for the case of the films grown with the O_3 oxidant compared to the films grown with the H_2O. The longer sputter time of the film grown with H_2O to reach the Si substrate in both the O and Si profiling coincides with the thicker film shown by the HRTEM. It was difficult to detect any notable change in the O profile by RTA due to the rather small signal intensity of O. However, there is a notable change in the Si profiles particularly at the interface region by RTA, as shown in Fig. 7(b).

As discussed earlier, the surface region hardly has any Si impurities. The Si profiles at interface regions show plateaus in the sputter-etching time region of 250–275 s and 240–270 s for the as-deposited HfO_2 films grown with the H_2O and O_3 oxidants, respectively. These time span become narrower after RTA. These plateaus are believed to correspond to the ILs of each sample. Between the IL and bulk of the films, where no Si is detected, there is a transition layer with a Si diffusion profile. These regions are believed to be the Hf silicate, and their thicknesses were estimated to be approximately 3 and 4 nm for the as-deposited films grown with the H_2O and O_3, respectively, from their respective Si concentration transient time. This result coincides very well with the many reports regarding Hf-silicate formation for the cases of thin ($<\sim 5$ nm) HfO_2 film deposition by ALD and other methods.[7,8,21] The film grown with the O_3 has a higher Si concentration both in the transition region and the IL before and after RTA compared to that of the film grown with H_2O. RTA increases the Si concentration in the IL by Si diffusion from the substrate for both cases. However, the Si concentration in the transition region of the film grown with H_2O does not increase at all whereas that of the film grown with O_3 increases by RTA. This might be due to the higher oxygen concentration of the film grown with the O_3, i.e., excess oxygen in the HfO_2 film offers an oxidation potential for the diffusing Si ions to form more Si–O bonds in the transition region (Hf silicate region). This increase in the Si concentration in the silicate region, in addition to the increase in the IL thickness, constitutes the reason for the larger increase in the CET by RTA for the case of the film grown using the O_3 oxidant (see Table I and Fig. 1). The higher Si concentration in the transition region can also be confirmed by the Hf $4f$ XPS signal of the thin (2–3 nm) films shown in Fig. 8. Figure 7(c) shows the SIMS depth profile results of Cl concentration. It can be understood that the Cl concentrations of the films show peaks at the interface for each case. However, the Cl concentrations in the film bulk are far lower for the case of the films grown with the O_3 oxidant compared to that of the film grown with the H_2O. RTA can greatly reduce the interfacial Cl contamination level but not the bulk Cl contamination. Therefore, using O_3 as an oxidant was crucial to obtain a low Cl contamination level.

Figure 8 shows the Hf $4f$ XPS spectra of the (a) as-deposited sample grown with H_2O, (b) postannealed sample

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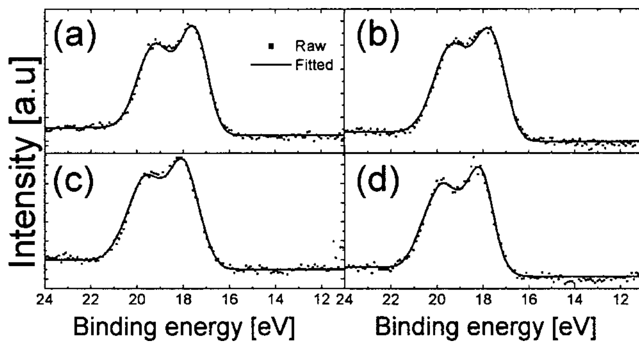

FIG. 8. Hf 4f XPS spectra of the (a) as-deposited sample grown with H_2O, (b) RTA sample grown with H_2O, (c) as-deposited sample grown with O_3, and (d) RTA sample grown with O_3.

grown with H_2O, (c) as-deposited sample grown with O_3, and (d) postannealed sample grown with O_3. The Hf 4f peak positions were calibrated using the Si substrate peak at 99.3 eV. The spectra were not deconvoluted. The rather high signal intensities in the binding energy region between the two Hf 4f peaks by the spin-orbital splitting ($4f_{7/2}$ and $4f_{5/2}$) suggest that the films were composed of HfO_2 and Hf silicate of which the Hf 4f peak binding energies were located at higher values. From the comparison between the Hf 4f peak positions from the as-deposited samples, it can be understood that these thin HfO_2 films grown with O_3 contains more Si compared to the film grown with H_2O. RTA at 950 °C shifts the peak positions to a higher binding energy by approximately 0.1 and 0.2 eV for the cases of the films grown with H_2O and O_3, respectively. This qualitatively coincides with the SIMS results for the Si concentration variations of the transition regions in the thick films.

Figure 9 shows the variation in the D_{it} as a function of the trap energy (E_T)—the intrinsic Fermi energy (E_i) of the various samples. The types of oxidants used during the growth primarily determine the D_{it}s of the samples. RTA at 750 °C has little effect on the D_{it}. The films grown with H_2O showed a D_{it} level $>10^{11}\,\mathrm{cm}^{-2}\,\mathrm{eV}^{-1}$, whereas the films grown with O_3 show mid- to low $10^{10}\,\mathrm{cm}^{-2}\,\mathrm{eV}^{-1}$ near the

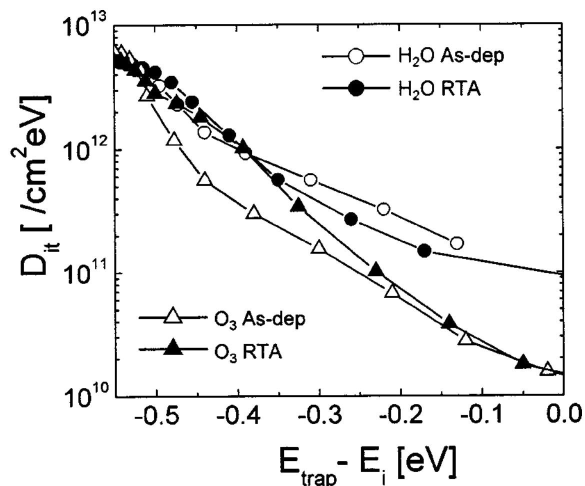

FIG. 9. Variation in the D_{it} as a function of the trap energy (E_T)—intrinsic Fermi energy (E_i) of the various samples.

mid gap. This low D_{it} level is close to that of the SiO_2/Si interface. Considering SiO_2 formation at the interface with Si for the case of the films grown with O_3, the small D_{it} is reasonable. This is a very important result since the high-k/Si interface almost always suffers from a high D_{it}.[2,11]

IV. CONCLUSIONS

HfO_2 gate dielectric thin films were deposited on Si wafers by an ALD method using $HfCl_4$ and either H_2O or O_3 as the precursor and oxidant, respectively. The stronger oxidation power of the O_3 compared to the H_2O increased the oxygen concentration in the HfO_2 film and interfacial SiO_2 formation, even at the as-deposited state. Because of the larger oxygen concentration, rapid thermal annealing at 750 °C under N_2 atmosphere produced a larger SiO_2 formation at the interface and Hf silicate formation than that of the HfO_2 film grown with H_2O oxidant. This results in a larger increase in the CET values compared to the HfO_2 film grown with the H_2O oxidant. Apart from this weakness, all the other electrical properties, including the fixed charge density, interface trap density, leakage current density, and hysteresis in the capacitance–voltage plot, of the film grown with O_3 were superior to those of the film grown with H_2O. In particular, the HfO_2 films grown with O_3 show a D_{it} level comparable to that of SiO_2/Si due to the presence of the interfacial SiO_2. Therefore, O_3 appears to be a better oxidant for the HfO_2 film growth using the ALD method considering both MOSFET and capacitor applications in memory devices.

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