Effects of ozone oxidation on interfacial and dielectric properties of thin HfO₂ films

L. Wang,¹ Paul K. Chu,¹,4) Andre Anders,² and Nathan W. Cheung³
¹Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
²Plasma Applications Group, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
³Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, California 94720, USA

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The effects of high concentration ozone oxidation at different temperatures on the interfacial and dielectric properties of thin HfO₂ films are examined. Analysis of the chemical shifts of the Hf 4f, Si 2p and O 1s core-level spectra acquired by x-ray photoelectron spectroscopy clearly indicates that the introduction of ozone can significantly improve the bonding characteristics between hafnium and oxygen even at low temperature. High-resolution cross-sectional transmission electron microscopy study shows that when the oxidation temperature is increased, film densification and crystallization occur at high temperature. The change in the dielectric properties of high temperature oxidation is analyzed and the results show that a negligible hysteresis and low fixed charge density can be achieved by medium temperature oxidation. When the oxidation temperature is increased to over 800 °C, the dielectric properties degrade due to regrowth of the interfacial layer and change in the film morphology. Our results also reveal that the leakage current can be reduced by high temperature ozone oxidation. © 2008 American Institute of Physics. [DOI: 10.1063/1.2976340]

I. INTRODUCTION

Due to the scaling of silicon complementary metal-oxide-semiconductor (MOS) devices, conventional SiO₂ can no longer be used for high performance sub-32 nm devices due to its unacceptable high leakage current.¹ Various kinds of high-k materials have been studied as potential replacements for SiO₂. Among them, Hf-based dielectrics such as HfO₂, HfSiO, and HfSiON have emerged as the preferred materials due to their reasonably high dielectric constant k, thermodynamic stability, and good interface quality with Si.² Although HfO₂ has been shown to possess superior electrical characteristics compared to other alternative gate dielectrics, the electrical properties of the HfO₂/Si interface need to be further improved and extensive efforts have been devoted toward improving the quality of this interface.³ Annealing at high temperature in the forming gas has been found to be effective in improving the interface quality by lowering both the interface state density and interface charges.⁴ Reduced point defect densities have also been observed by increasing the annealing temperature up to 1000 °C.⁵ Several reports have shown that ozone oxidation is a rapid and more effective process in achieving high quality SiO₂.⁶,⁷ Other recent reports have also shown that high quality thin HfO₂ films can be produced by ultraviolet ozone oxidation of Hf metal films deposited by physical vapor deposition.⁸,⁹ In our previous study, it was demonstrated that a Hf-silicate interfacial layer between the HfO₂ film and silicon substrate can be effectively controlled by ozone oxidation.¹⁰

In the work reported in this paper, we analyze the effects

II. EXPERIMENTAL DETAILS

The HfO₂ samples were prepared by oxidation of evaporated Hf metal films on silicon substrates under a high concentration of ozone at different temperatures. P-type Si (100) wafers with a resistivity of 1–2 Ω cm were first cleaned by diluted HF (1:10). The Hf metal films were deposited by e-beam evaporation under high vacuum (2 × 10⁻⁸ Torr) without intentional heating. After metal deposition, the samples were transferred to a home-made furnace and densified under N₂ with 5% H₂. Afterwards, a high concentration of ozone (3%) produced by a commercial ozone generator was introduced and oxidation was performed under 1 atm pressure for 300 s.¹⁰ HfO₂ samples oxidized using the same experimental parameters but under pure oxygen were also prepared for comparison. The chemical composition and binding energy of the samples were determined by x-ray photoelectron spectroscopy (XPS) and Rutherford back-scattering spectrometry (RBS). XTEM was used to characterize the interfacial properties. The capacitance-voltage
(C-V) curves were acquired on an HP4284A precision LCR meter and current-voltage (I-V) curves were obtained on an HP4145B semiconductor parameter.

III. RESULTS AND DISCUSSION
A. Interfacial characteristics of ozone oxidized HfO2 thin films

Figure 1 shows the XPS spectra of the HfO2 films oxidized by ozone (denoted as ozone HfO2) and under oxygen (denoted as oxygen HfO2) at different temperatures. Prior to the analyses, about 1 nm of the top layer was removed by 4 keV Ar ion bombardment to remove surface contaminants. The Hf 4f core-level spectra of the three ozone HfO2 samples show only a Hf 4f7/2 peak at a binding energy of 17.6 eV which corresponds to the Hf–O bond in bulk HfO2.11 On the other hand, the oxygen HfO2 sample oxidized at 150 °C shows two noticeable but small shoulders highlighted by the arrows at the lower binding energy side of the main peak, as shown in Fig. 1a. It can be attributed to the Hf–Si bond as a result of oxygen deficient oxidation and formation of Hf-silicide.12 When the oxidation temperature is higher than 450 °C, only the Hf–O bond is detected from both the oxygen and ozone HfO2 samples indicating full oxidation at high temperature.

In the Si 2p core-level spectra shown in Fig. 2, the main peak appears at 99.3 eV which is the binding energy of bulk Si. In low temperature oxidation, only the oxygen HfO2 sample shows a shoulder at about 102.2 eV in the Si 2p spectra. This implies a more silicatellite nature at the interface between the HfO2 and H-terminated Si substrate under low temperature oxygen oxidation.13 No Si–O bond is detected from the ozone HfO2 sample at low temperature. When the oxidation temperature is higher than 450 °C, both the oxygen and ozone HfO2 Si 2p spectra exhibit a broadened peak at about 102.5 eV, which may comprise two components of Hf silicate and SiO2(Si4+) at the dielectric-semiconductor interface.14 As the oxidation temperature is increased to 800 °C, a strong peak emerges at about 103.2 eV from both the oxygen HfO2 and ozone HfO2 samples, implying that SiO2 is the main component of the interfacial layers in the samples oxidized at high temperature.

To further determine the oxygen profile near the interface after low temperature oxidation, XPS depth profiling is conducted by monitoring the O 1s core-level peak. The results are displayed in Fig. 3. In Fig. 3a, a sizable shift of about 1.2 eV can be observed after pure oxygen oxidation. This shift can be assigned to the formation of Hf silicate and partial oxidation of oxygen HfO2.11 According to the O 1s peak of the ozone HfO2 sample, no obvious shift can be observed between the silicon substrate and interface as shown in Fig. 3b. This implies that very little Hf silicate has been formed at the interface after ozone oxidation even at a low temperature of 150 °C. We believe that the results are in part due to the high electron affinity of ozone and its
decomposition into atomic O which is chemically more active. At the same time, no increase in the oxygen concentration with respect to hafnium concentration can be detected by RBS by comparing the ozone HfO2 with oxygen HfO2 samples. This clearly indicates that the introduction of ozone can significantly improve the bonding characteristics between hafnium and oxygen at low temperature.

Figure 4 shows the high-resolution XTEM images of the ozone oxidized HfO2 samples at different temperatures. No noticeable interfacial layer can be observed from the low temperature ozone HfO2 sample as shown in Fig. 4(a), which indicates that the layer-by-layer growth mode is predominant in the formation of homogenous hafnium oxides. A relatively thick interfacial region about 1.2 nm in thickness can be observed from the 450 °C oxidized ozone HfO2. The interfacial layer thickness increases to about 1.8 nm in the high temperature oxidized sample. Our results show that when the oxidation temperature is increased, the HfO2 layer densifies. In addition, according to the XPS spectra, Hf atoms diffuse into the interfacial region to form a Hf-silicate-like interfacial layer. It can also be observed from the figure that the HfO2 film is crystallized during high temperature oxidation. The crystallization temperature is believed to be above 900 °C but the actual local crystallization temperature is much lower. This difference may be due to the existence of impurities or some nucleation centers.

B. Dielectric properties of ozone oxidized HfO2 thin films

In order to investigate the effects of high temperature annealing on gate dielectric properties, circular MOS capacitors are fabricated using gold top electrodes with a diameter of 200 μm. A gold film is deposited onto the back side of MOS capacitors for better electrical contact. The gate voltage is swept from inversion to accumulation and back in order to check the magnitude of hysteresis. Figure 5(a) shows the C-V characteristics of the HfO2 samples oxidized in oxygen at different temperatures. The sample oxidized at a low temperature (150 °C) exhibits large hysteresis of about 130 mV, implying a high density of charge trapping centers. When the oxidation temperature is increased to 450 °C, the hysteresis diminishes to about 30 mV. A negligible C-V hysteresis of about 5 mV is obtained after 800 °C annealing. The hysteresis is mostly due to slow interface states as UHV evaporation significantly reduces mobile ion charges in the deposited films. At the same time, the accumulation capacitance shows the highest value when the oxidation temperature is around 450 °C and it decreases to only 100 pF after oxidation at 800 °C. It is believed that the significant increase in the thickness of the interfacial layer is the main reason for the reduced accumulation capacitance. The flat-band voltage of the 800 °C oxidized sample also shifts to the right by about 350 mV, which indicates the change in the fixed charge density. The density of the fixed negative charge calculated is on the order of $10^{12}$ cm$^{-2}$, which is caused by the change in film morphology.

To compare to the samples oxidized in oxygen, Fig. 5(b) shows the C-V characteristics of the HfO2 samples oxidized in ozone at different temperatures. All three samples consistently show negligible hysteresis (less than 10 mV) thereby suggesting much smaller densities of charge trapping centers in the ozone oxidized samples. This is because ozone oxidation can significantly reduce dangling bonds and oxygen vacancies in the oxide films. The accumulation capacitance dis-

FIG. 4. High-resolution XTEM micrographs of ozone HfO2 at oxidation temperatures of (a) 150 °C, (b) 450 °C, and (c) 800 °C.

FIG. 5. (Color online) C-V curves measured from the Au/HfO2/Si MOS capacitors after oxidation under (a) oxygen and (b) ozone, measured at a frequency of 1 MHz.
plays the same trend as the oxygen oxidized samples, in that the maximum value is achieved when the annealing temperature is around 450 °C. The flatband voltage shift study also shows that the lowest density of fixed charges is obtained when the oxidation temperature is around 450 °C.

Figure 6 shows the J-V characteristics of the ozone oxidized HfO2 samples at the equivalent oxide thickness (EOT) of about 1.25 nm. The asymmetry in the J-V curve is attributed to the difference in the physical properties and conduction mechanisms across the Au/HfO2 and HfO2/Si interfaces. The leakage current densities measured at $|V_{GS} - V_{FB}| = 1$ V are $3.5 \times 10^{-3}$ A/cm² for the HfO2 samples oxidized in ozone at low temperature. When the oxidation temperature is increased to 800 °C, the value diminishes drastically to about $1.2 \times 10^{-5}$ A/cm². It is clear that all these values are significantly smaller than that of SiO2 at the identical EOT. Moreover, the ozone oxidized sample shows an improvement by two orders of magnitude compared to the oxygen oxidized sample. It is believed that the strong Hf–O bond and less oxygen vacancies remove the electron leakage path, then, atomic oxygen can occupy the oxygen vacancies, thus, hindering the conduction of leakage electrons.17

IV. CONCLUSION

High concentration ozone oxidation is an effective way to improve the bonding characteristics between hafnium and oxygen even at low temperature. XTEM indicates that when the oxidation temperature is increased, the HfO2 films densify and the microstructure changes from amorphous to polycrystalline. Electrical studies show changes in the dielectric properties of HfO2 at different temperatures. A negligible hysteresis of about 5 mV and low fixed charge density can be achieved by ozone oxidation at medium temperature. When the oxidation temperature is increased to over 800 °C, the dielectric properties degrade due to regrowth of the interfacial layer and changes in the film morphology. Our results also reveal that the leakage current can be reduced by high temperature ozone oxidation.

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