Control of interfacial silicate between HfO_2 and Si by high concentration ozone

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By high concentration ozone oxidation at low temperature, the Hf-silicate interfacial layer between HfO_2 and silicon substrate is effectively controlled. This is evident by investigating the chemical shifts of the Hf $4f$ and Si $2p$ core-level spectra with depth by using x-ray photoelectron spectroscopy. The improved interfacial microstructure is further confirmed by high-resolution cross-sectional transmission electron microscopy. The capacitance-voltage curves, obtained from the metal-oxide-semiconductor capacitors using the ozone oxidized HfO_2 as the gate dielectric, show a negligible hysteresis of about 5 mV and a low fixed charge density. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2173708]

Various kinds of high-k materials are currently under consideration as potential replacements for SiO_2 as gate dielectric materials in future complementary metal-oxide-semiconductor (MOS) technology.[1] Among them, HfO_2 and ZrO_2 have emerged as the preferred oxides due to their reasonably high dielectric constant k, thermodynamic stability, and good interface quality with Si.[2] However, an interfacial layer, either the growth of silicon oxide or the formation of Hf silicate ($Hf_xSi_yO_4$) or Hf silicide (Hf_xSi_y), can be easily formed during the deposition of HfO_2 on silicon, thereby canceling the benefits of high dielectric constant. Therefore, the control of the interfacial layer in high permittivity gate dielectrics is critical to the use of the materials in microelectronic devices. Copel *et al.*[3] believe that silicate formation is not a significant factor for samples prepared by molecular-beam epitaxy and chemical vapor deposition. Lee *et al.*[4] claim that, for atomic layer deposited HfO_2, the interfacial layer is mainly silicon oxide or suboxide. Renault *et al.*[5] conclude that Si-rich Hf silicate exists in their samples by analyzing the energy shift of the interfacial components. Copel *et al.*[6] indicate that SiO_2 decomposes and reacts with HfO_2 during deposition; and Wang *et al.*[7] also observe the same phenomena. The decomposition and reaction of SiO_2 produce an interfacial transition region containing hafnium and silicon. These results are often confused when attempts are made to control the formation of the interfacial layer. To avoid such confusion, it is necessary to understand and control the formation of interfacial silicate layers so that HfO_2 films can actually be used as a dielectric film for microelectronic devices.

In this letter, we report on the control of the interfacial silicate layer between HfO_2 and silicon substrate by introducing high concentration ozone oxidation. Previously, ozone oxidation was found to be useful for producing high-quality SiO_2 on Si with a low charge trap density and excellent interface at low temperature.[8,9] Furthermore, high-purity thin HfO_2 film produced on silicon with chemically grown SiO_2 has been demonstrated by ultraviolet ozone oxidation of physical-vapor-deposited Hf metal. However, the chemical reactions between HfO_2 and silicon have seldom been reported in literature.[10,11]

HfO_2 samples were prepared by oxidation of evaporated Hf metal films on a silicon substrate in high concentration ozone at low temperature. p-type Si (100) wafers with a resistivity of $1-2\ \Omega$ cm were used and first cleaned by diluted HF (1:10). The Hf metal films were deposited by electron-beam evaporation under a high vacuum (2×10^{-8} Torr) without any intentional heating. After metal deposition, the samples were transferred to a home-made furnace and densified under N_2 with 5% H_2. Then, high concentration ozone (3%) produced by a commercial ozone generator was introduced and oxidation was performed at 150 °C for 5 min under 1 atm partial pressure. Another HfO_2 sample was oxidized using the same experimental parameters, but under pure oxygen for comparison. The chemical composition and binding energy of the samples were determined by x-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS). High-resolution cross-sectional transmission electron microscopy (XTEM) was used to characterize the interfacial properties. Capacitance-voltage (C-V) curves were acquired by HP4284A precision LCR meter.

Figure 1 shows the XPS spectra of the HfO_2 film oxidized by ozone (denoted as ozone HfO_2 here), the HfO_2 film oxidized under oxygen (denoted as oxygen HfO_2) and the as-deposited Hf metal film. Prior to the analyses, about 1 nm of the sample top layer was removed by 4 keV Ar ion bombardment to remove surface contaminants. The Hf $4f$ core-level spectrum of ozone HfO_2 only shows a Hf $4f_{7/2}$ peak at a binding energy of 17.6 eV which corresponds to the Hf–O bond in bulk HfO_2;[5] whereas in oxygen HfO_2, two noticeable but small shoulders (highlighted by the arrows) at the lower binding energy side of the main peak are observed as shown in Fig. 1(b). It can be attributed to the Hf–Si bond as a result of oxygen deficient oxidation and formation of

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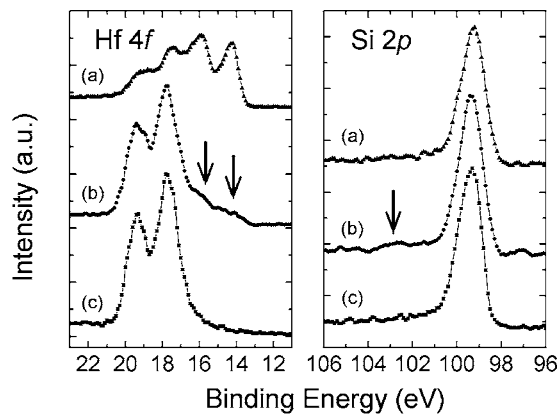

FIG. 1. Hf 4f and Si 2p core-level spectra acquired by XPS from: (a) As-deposited Hf metal, (b) oxygen HfO_2, and (c) ozone HfO_2.

Hf-silicide.[12] In contrast, an intense peak at 14.2 eV appears in the Hf 4f core-level spectrum acquired from the as-deposited Hf metal, as shown in Fig. 1(a), which corresponds to the strong Si–Hf bond in pure Hf metal. Furthermore, a shoulder at a binding energy of 17.4 eV is also detected that arises from the Hf–O bond in HfO_2 or $(HfO_2)_x(SiO_2)_{1-x}$.[11] This presumably results from partial oxidation of the as-deposited Hf metal, mostly occurring after removal from the vacuum chamber and exposure to air. With regard to the Si 2p core-level spectra, the main peak appears at 99.3 eV which is the binding energy of the bulk Si. Only oxygen HfO_2 shows a shoulder at about 102.2 eV in the Si 2p spectra. This implies a more silicate-like nature at the interface between the HfO_2 and H-terminated Si substrate.[13] No increase in the oxygen concentration with respect to hafnium concentration can be detected by RBS, in comparison of ozone HfO_2 with oxygen HfO_2. This clearly indicates that the introduction of ozone can significantly improve the bonding nature between hafnium and oxygen.

To further determine the compound composition near the interface, XPS depth profiling using the Hf 4f core-level peak was conducted and the results are shown in Fig. 2. In Fig. 2(a), a sizable shift of about 1.2 eV appears after pure oxygen oxidation. This shift can be assigned to the formation of Hf-silicate.[5] Meanwhile, strong Hf–Si bonds can even be detected at the lower binding energy of about 13.6 eV with increasing depths. This further corroborates the partial oxidation of the oxygen oxidized sample, as well as formation of both Hf-silicate and Hf-silicide near the interface, which have also been observed by Wang *et al.*[7] For the Hf 4$f_{7/2}$ peak of ozone HfO_2, no obvious shift can be observed from the silicon substrate to the interface as shown in Fig. 2(b). This means very little Hf-silicate has been formed at the interface after ozone oxidation. We believe that the results here are, in part, due to the high electron affinity of ozone and its decomposition to atomic O which is chemically more radical.

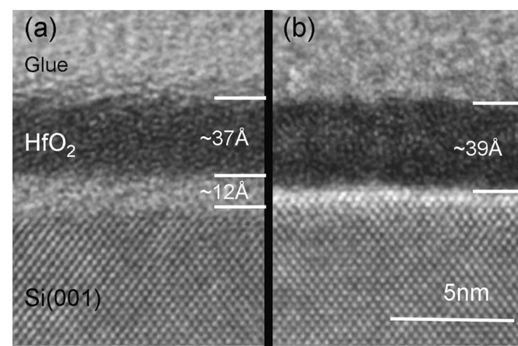

FIG. 3. High-resolution XTEM micrographs of: (a) oxygen HfO_2 and (b) ozone HfO_2.

Figure 3 shows the high-resolution XTEM images of both the oxygen and ozone oxidized HfO_2 samples. The oxygen HfO_2 sample in Fig. 3(a) has a high interface roughness compared with that prepared by ozone. About a 12 Å thick silicate-like interfacial region appears, and the results are in agreement with the Si 2p XPS spectra. In contrast, the ozone oxidized sample shown in Fig. 3(b) exhibits a sharp interface between the HfO_2 and Si substrate and no noticeable interfacial layer can be observed. This is considered to be due to the reduction of interfacial Si displacement during ozone oxidation and the layer-by-layer growth mode is predominant to form the homogenous hafnium oxides.[14]

In order to investigate the effects of high concentration ozone oxidation on the gate dielectric properties, circular MOS capacitors were fabricated with aluminum gate electrodes. Also an aluminum film was deposited on the back side of the MOS capacitors for better contact. The gate voltage was swept from inversion to accumulation and back to check the magnitude of hysteresis. As shown in Fig. 4, the ozone HfO_2 shows excellent C-V characteristics indicating negligible C-V hysteresis ($\sim$5 mV). This again demonstrates that ozone oxidation after Hf deposition is beneficial to the improvement of the interface properties and reduction of the charge trapping centers, compared to HfO_2 oxidized in pure

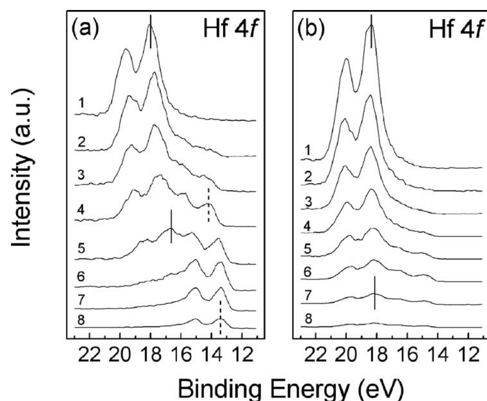

FIG. 2. XPS depth profile montage of Hf 4f core-level acquired every 20 s from: (a) oxygen HfO_2 and (b) ozone HfO_2.

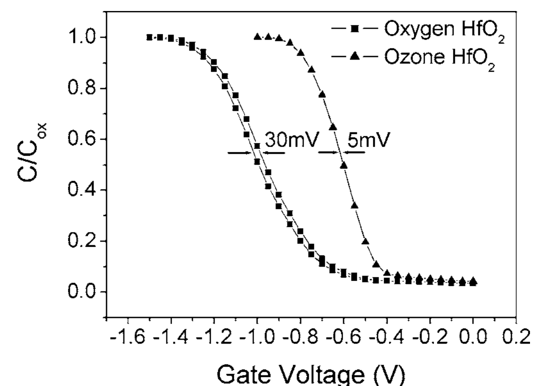

FIG. 4. C-V curves measured from the Al/HfO_2/Si MOS capacitors after oxidation under ozone or oxygen measured at a frequency of 1 MHz.

oxygen. The density of the fixed positive charge calculated from the flat-band voltage shift is on the order of 10^{11} cm^{-2} for ozone HfO_2, and this value is one order of magnitude better than that of the oxygen oxidized sample.

In summary, interfacial silicate formation between HfO_2 and silicon can be controlled by high concentration ozone oxidation, and improved interfacial composition and microstructure are achieved. Our electrical study shows that the ozone oxidized sample has superior dielectric properties, as manifested by the negligible hysteresis and low fixed charge density.

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