Effects of plasma immersion ion nitridation on dielectric properties of HfO$_2$

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Plasma immersion ion nitridation is used to produce thin HfO$_2$ films with improved thermal and electrical properties. The film composition is investigated by examining the chemical shifts of the Hf 4f, Si 2p, and N 1s core-level spectra using x-ray photoelectron spectroscopy. The improved thermal stability and interfacial microstructure are further confirmed by high-resolution cross-sectional transmission electron microscopy. Electrical studies show an equivalent oxide thickness of about 1.25 nm, a negligible hysteresis of about 5 mV, and a low fixed charge density. © 2007 American Institute of Physics. [DOI: 10.1063/1.2715044]

Various kinds of high-$k$ materials are currently under consideration as potential substitutes for SiO$_2$ as the gate dielectric in future complementary metal-oxide-semiconductor technology. Among them, HfO$_2$ and ZrO$_2$ have emerged as the preferred materials due to their reasonably high dielectric constant $k$, thermodynamic stability, and good interface quality with Si. HfO$_2$ films can be formed by using several methods such as atomic layer deposition, chemical vapor deposition, sputter deposition of Hf metal followed by annealing, and reactive sputtering. However, an interfacial layer, either SiO$_2$ or Hf silicate/silicide, can be easily formed during the deposition of HfO$_2$ on silicon and thermal stabilities of these samples must be improved. It is imperative to control the interfacial layer growth and improve the thermal stability at the same time. Our previous study shows that by high concentration ozone oxidation at low temperature, the Hf silicate interfacial layer between the HfO$_2$ and silicon substrate can be effectively controlled. Another problem encountered in high-$k$ study is the thermodynamic stability after high temperature postdeposition annealing. One common way to address this issue is to incorporate nitrogen into the high-$k$ films. Previous approaches include nitridating the film in subsequent annealing in NH$_3$ or N$_2$ ambient after metal oxide formation or incorporating nitrogen during sputtering under a N$_2$ flow. These methods tend to improve the thermal stability properties and reduce the leakage current but do not solve the interfacial problems. Plasma nitridation has been shown to be an effective method to improve the thermal and electrical properties of high-$k$ dielectrics. In this letter, a technique to produce thin HfO$_2$ films with improved thermal and electrical properties is proposed by combining high concentration ozone oxidation and plasma immersion ion nitridation.

$p$-type Si (100) wafers with a resistivity of 1–2 Ω cm were used and first cleaned by diluted HF (1:10). Hf metal films were deposited by e-beam evaporation under high vacuum ($2 \times 10^{-8}$ torr) without intentional heating. After metal deposition, the samples were nitrided in a plasma immersion configuration by applying a bias of −100 V to the samples for 1–2 h. The plasma nitridation time determines the film thickness. Because this is a low-energy process, nitrogen is mainly incorporated into the film by diffusion. Afterwards, high concentration ozone (3%) produced by a commercial ozone generator was introduced and oxidation was performed in a tube furnace at 150 °C for 5 min under 1 atm partial pressure. Rapid thermal annealing (RTA) was finally performed at 1000 °C for 30 s.

Figure 1 depicts the x-ray photoelectron spectroscopy (XPS) Hf 4f and Si 2p core-level spectra of the HfO$_2$ films with and without nitrogen incorporation. Prior to the analyses, about 3 nm of the sample surface were removed by 4 keV Ar ion bombardment to remove surface contaminants. The spectrum acquired from the HfO$_2$ without nitrogen incorporation 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$_2$. The main peak of the nitrided sample shifts to a lower binding energy of about 17.3 eV due to the presence of nitrogen in the film. With regard to the Si 2p core-level spectra, the

![Figure 1: XPS Hf 4f and Si 2p core-level spectra acquired from the HfO$_2$ samples with and without nitrogen incorporation. The arrows indicate the two possible shoulder peak positions.](image-url)
main peak appears at 99.3 eV which is the binding energy of bulk Si. A shoulder (highlighted by the arrow) at about 102.6 eV can be observed in the Si 2p spectra of the sample without nitridation indicating the formation of a Hf silicate interfacial layer. The shoulder peak of nitrided sample shifts to a lower binding energy of about 102.0 eV on account of the Si–N bond at the interface between the HfO2 and Si substrate. The Hf 4f and Si 2p core-level spectra show that the interfacial region contains both Hf–Si–O and Si–N bonds.

Figure 2 displays the XPS N 1s core-level spectra of the plasma-nitrided HfO2 samples before and after RTA. The quantity of N incorporated into the film is determined to be about 6 at. % before RTA and reduced to about 3 at. % afterwards. Before RTA, the main peak which is not a Gaussian contains several overlapping peaks. One shoulder peak appears at 397.8 eV attributable to N–Hf bonds. Another peak at about 401.5 eV is caused by molecular N2 or gaseous NOx. It is likely that these N atoms are in the interstitial sites or bound to interstitial O atoms. A broad peak also appears in the N 1s spectrum of the plasma-nitrided HfO2 after RTA, but due to insufficient energy resolution of the instrument, the individual peaks cannot be resolved unambiguously. Nevertheless, the peak at 401.5 eV diminishes significantly implying breakage of the N–O bonds during annealing. It has been reported that some of the N atoms move around in the dielectric to form N–Hf bonds.

Figure 3 shows the high-resolution cross-sectional transmission electron microscopy (XTEM) image of plasma-nitrided HfO2. All the nitrogen incorporated samples exhibit an amorphous microstructure. The HfO2 sample without nitrogen incorporation crystallizes after rapid thermal annealing, whereas the plasma-nitrided HfO2 retains the amorphous structure even after RTA at 1000 °C for 30 s. This is a good indication of the improved thermal stability of HfO2 after nitrogen incorporation. It is believed that nitrogen can lead to a decrease in the average atomic coordination, thereby helping to increase the resistance to crystallization and the ability to withstand high temperature processing. By optimizing our experimental parameters, the interfacial layer thickness can be reduced to about 0.6 nm in the sample shown. Based on the XPS study described above, the composition of the interfacial layer is most likely HfSiON, which has a higher dielectric constant than SiO2 and will benefit the overall dielectric properties of the film.

In order to investigate the effects of nitrogen incorporation on the gate dielectric properties, circular metal-oxide-semiconductor (MOS) capacitors were fabricated with gold gate electrodes. 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. For comparison, capacitance-voltage (C-V) curves were also obtained from the HfO2 samples without nitrogen incorporation. As shown in Fig. 4, the sample without nitrogen incorporation exhibits a large hysteresis of about 130 mV suggesting a high density of charge trapping centers. The density of the fixed positive charge calculated from the flatband voltage shift is on the order of 1012 cm−2. In contrast, the plasma-nitrided HfO2 sample shows excellent C-V characteristics with negligible C-V hysteresis (∼5 mV) and small flatband voltage shift. The calculated equivalent oxide thickness is about 1.25 nm for a HfO2 film with a physical thickness of 5.5 nm. The inset figure in Fig. 4 compares the J-V characteristics between the plasma-nitrided HfO2 sample and HfO2 sample without nitrogen incorporation. The leakage current density of the HfO2 without nitrogen incorporation measured at $V_{GS} - V_{FB} = 1$ V is as high as 0.05 A/cm². After plasma nitridation, the leakage current density drastically diminishes to 3.2 × 10−5 A/cm². It is clear that plasma nitridation can...
significantly reduce the leakage current by three to four orders of magnitude. The improvement is believed to be due to the fact that the incorporated nitrogen atoms can occupy the oxygen vacancies and hinder the conduction of leakage electrons.\textsuperscript{16}

HfO\textsubscript{2} samples nitrided using traditional ion implantation are also examined for comparison. Although the leakage current density of high dose ion-implanted HfO\textsubscript{2} sample is reduced to $1.5 \times 10^{-5}$ A/cm\textsuperscript{2}, which is better than that of the plasma-nitrided sample, there exist some interfacial states and charge trapping centers as observed from the C-V curves. First principle simulation shows that the band gap decreases with increasing N concentration due to the extension of the N 2\textit{p} state into the band gap.\textsuperscript{17} Another effect of high dose ion implantation is that if the incorporated nitrogen amount exceeds a reasonable value, some nitrogen atoms will occupy the interstitial sites and cause instability when the gate stack is subjected to electron irradiation. Our previous XTEM study has shown that the microstructures of these samples change from amorphous to polycrystalline during short-time electron irradiation.\textsuperscript{18}

In summary, thin HfO\textsubscript{2} films with improved electrical and thermal properties have been produced by low-energy plasma immersion ion nitridation. XTEM shows that the plasma-nitried HfO\textsubscript{2} retains an amorphous microstructure even after RTA at 1000 °C. Electrical measurements show that the leakage current density is reduced by three to four orders of magnitude after nitrogen incorporation, while other favorable properties such as negligible hysteresis and a low fixed charge density are also accomplished.

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