Electrical characteristics of ultrathin Hafnium oxynitrides deposited on Si-substrate

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Abstract

Hafnium oxide and Hafnium oxynitrides thin films are deposited on a Si substrate using reactive sputtering. Compared with Hafnium dioxide, Hafnium oxynitrides showed excellent electrical characteristics such as low leakage current density and low capacitance equivalent oxide thickness. By X-ray photoelectron spectroscopy (XPS), we were able to confirm nitrogen incorporation in the oxide bulk and at the Si-HfO$_x$N$_y$ interface, which can repel the Si-O bonding in comparison with Hafnium oxide. It provides the adequate evidence to support the improved electrical characteristics.

Key words: Hafnium oxide; I-V; C-V; XPS

1. Introduction

The development of 0.1 $\mu$m metal-oxide-semiconductor field-effect transistor (MOSFET) devices in year of 2005 is predicted. By considering a semiconductor industry association (SIA) technology roadmap, a gate oxide thickness of less than 15Å will be required for using in 0.1 $\mu$m MOSFET applications. Due to the excess of direct tunneling leakage current of SiO$_2$ at the thickness below 15Å, thermal SiO$_2$ is not applicable for gate oxide application [1, 2]. Therefore, it is necessary to develop an alternative to SiO$_2$ with excellent electrical characteristics such as high dielectric constant, low leakage current density, low interface state density and good thermal stability [3, 4]. Among various high-$k$ gate dielectrics, HfO$_2$ films have also been investigated as an alternative gate dielectric. Recently, Matsuo et al. proposed a new method of depositing TiO$_2$ on silicon. It was also reported that a significant improvement in leakage current and trap density was obtained using nitrogen incorporation in ZrO$_2$ and Ta$_2$O$_5$ films. In this paper, we report on the excellent thermal stability and electrical characteristics of Hafnium oxynitride film, which was simply prepared by sputtering and was directly deposited on silicon [5, 6].

2. Experimental
Silicon wafers used in this experiment were 3 in. diameter, n-type Czochralski Method (CZ) with (100) orientation. Wafer resistivity was in the 1.0-10.0 Ω cm range. After standard cleaning with final HF dip, HfO₂ and HfOₓNᵧ gate dielectric were grown by sputtering at room temperature. Then, the samples were annealed at temperatures of 550°C and 800 °C, respectively. Finally, the samples were fabricated with Al top and bottom electrode, respectively. Electrical measurements were performed using a probe station located inside a metal box to provide insulation from electromagnetic interference. Capacitance and conductance (C-G-V) and admittance measurements were made via a computer-controlled Keithley 590 C-V analyzer at 1 MHz and a test signal of 15 mVrms. Current-voltage (I-V) characteristics were measured using a Keithley 236 voltage source.

3. Results and Discussion

The C-V measurements on HfOₓNᵧ and HfO₂, obtained at 1 MHz, are shown in Fig. 1 (a) and (b). The samples represent in figure are those before annealing, as well as annealing at a temperature of 550 °C and 800 °C. The curves were obtained on dots with an area of 4.91x10⁻⁴ cm², under forward and backward sweeps. The C-V curves obtained on both sets of samples, HfOₓNᵧ and HfO₂ films, show shoulders and significant hysteresis. The HfOₓNᵧ films with an EOT of about 17Å (at 550 °C) and the HfO₂ films with an EOT of about 28.5 Å (at 550°C) were calculated using accumulation capacitance values as shown in the Fig. 1(a) and 1(b). Consequently, we found that the capacitance of HfOₓNᵧ is much larger than HfO₂.

![C-V curves](image1)

![C-V curves](image2)

Fig.1. The measurements of C-V curves at different annealing temperatures of 500°C and 800 °C as well as non-annealed samples for (a) HfO₂ and (b) HfOₓNᵧ.

The leakage currents were measured from -2V to 2V in a metal box, as shown in Fig. 2 (a) and (b). After annealing, the leakage currents were smaller than before annealing. Furthermore, the leakage currents of HfOₓNᵧ films were four orders less than the HfO₂ ones. Nevertheless, we also
found that the leakage current decreased with the increasing of annealing temperature. The improvement in leakage currents can be explained by the low trap density due to the nitrogen incorporation. The improvement in EOT can be explained by the reducing for interfacial oxidation due to the nitrogen incorporation. 

which are consistent with the formation of the silicate film. Besides, the bonding of Hf-Si is not expected in the HfO$_2$ and HfO$_x$N$_y$ films. The depth of the O1s spectra are shown in Fig. 4.

![Fig. 2. The measurements of I-V curves at different annealing temperatures of 500°C and 800 °C as well as non-annealed samples for (a) HfO$_2$ and (b) HfO$_x$N$_y$.](image1.png)

![Fig. 3. Hf4f XPS spectra from (a) HfO$_2$ film. (b) HfO$_x$N$_y$ film. The features’ difference is due to the annealing temperature, which deposited directly on the Si substrate.](image2.png)
the binding energy of 530 eV. It indicates that the interface layer has been decomposed by the diffusion of the silicon atoms, resulting in the decrease of dielectric constant as well as the thermal instability. Once annealing the films at 800 °C, the peak of about 535 eV dominates, while the 532 eV still remained, which is associated with the bonding of Si-O-Si and the annihilation of O-H bonding, respectively. However, the silicate bonding is responsible for the poor electrical characteristics. Therefore, the results exhibit an adequate evidence that the hafnium oxide treated at a temperature higher than 500 °C will reduce the thermal stability. Compared with the Fig. 4.(b), we could find that the peak move in the positive direction (towards right the figure) of binding energy for the HfO\textsubscript{x}N\textsubscript{y} films, which explain that the bonding of the silicate layer is Si-Hf-O-N. The incorporation of nitrogen not only reduce the bonding of Si-O-Si and Hf-O-H, but also fetch the silicon atoms. Moreover, the interface layer thickness was significantly suppressed, and was kept almost the same EOT in comparison with non-annealed samples, which was also confirmed by the C-V curves.

Fig. 5.(a) and (b) show the XPS Si\textsuperscript{2p} spectra for analyzing the chemical composition of the HfO\textsubscript{2} and HfN\textsubscript{x}O\textsubscript{y}, in which a feature of double peaks was shown. By compared with Fig.5.(a) and Fig.5.(b), they both showed minor peak at about 99 eV, which is corresponding to the Si-Si bonding, but the major peak is different. The one at 103.3 eV of fig. 5.(a) is related to the Si-O bonding, while the other at 101.8 eV of fig. 5.(b), is consistent with the Si-N bonding for annealing temperature at 800 °C. The results also confirm the importance of nitrogen, which will enhance the charge retention, decrease the EOT in conjunction with the silicon atoms, and also upgrade the thermal stability and electrical characteristics.

The EOT and optical thickness of
HfO$_2$ and HfO$_x$N$_y$ films were shown in Fig. 6 (a) and 6 (b), respectively. The HfO$_x$N$_y$ films were more stable than HfO$_2$, which was due to fact that the nitrogen incorporate with HfO$_x$N$_y$. Furthermore, the HfO$_x$N$_y$ could not effectively increase the EOT at high annealing temperature. It is found that HfO$_x$N$_y$ films have good thermal stability.

**Conclusion**

In this paper, we investigated the HfO$_x$N$_y$ and HfO$_2$ films prepared by sputtering. Compared with the HfO$_2$ films, the HfO$_x$N$_y$ films showed significant improvements such as a leakage current density of less than 1 $\mu$A/cm$^2$. In addition, the EOT of about 17 Å and superior thermal stability were confirmed for HfO$_x$N$_y$ films. By XPS analysis, we were able to confirm the nitrogen incorporation in HfO$_x$N$_y$ and HfO$_2$.
the formation of interfacial SiO$_x$N$_y$, where the Si-N bonding was confirmed at a annealing temperature of 800 °C. Furthermore, the HfO$_x$N$_y$ could not effectively increase the EOT at high annealing temperature.

Reference: