Electrical characteristics of ultrathin Hafnium oxynitrides deposited on Si-substrate

Jun-Yuan Chen, Jung-Chuan Chou, Hsueh-Tao Chou, Shu-Cheng Fang
Institute of Electronic Engineering, National Yunlin University of science & Technology, 123, section 3, University Road, Touliu, Yunlin, Taiwan, R. O. C.
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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_xN_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

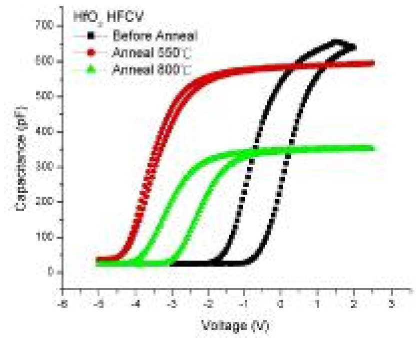
The development of 0.1 μm metal-oxide-semiconductor field-effect transistor (MOSFET) devices in year of 2005 is predicted. By considering a semiconductor industry association (SIA) technology roadmap, a gate oxide thickness of less than 15Å will be required for using in 0.1μm MOSFET applications. Due 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_2O_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 Ωcm range. After standard cleaning with final HF dip, HfO_2 and HfO_xN_y gate dielectric were grown by sputtering at room temperature. Then, the samples were annealed at temperatures of 550℃ and 800℃, 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 mV_{rms}. Current-voltage (*I-V*) characteristics were measured using a Keithley 236 voltage source.

3. Results and Discussion

The C-V measurements on HfO_xN_y and HfO_2, 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 ℃ and 800 ℃. The curves were obtained on dots with an area of 4.91×10^{-4} cm^2, under forward and backward sweeps. The C-V curves obtained on both sets of samples, HfO_xN_y and HfO_2 films, show shoulders and significant hysteresis. The HfO_xN_y films with an EOT of about 17Å (at 550 ℃) and the HfO_2 films with an EOT of about 28.5 Å (at 550℃) were calculated using accumulation capacitance values as shown in the Fig. 1(a) and 1(b). Consequently, we found that the capacitance of HfO_xN_y is much larger than HfO_2.



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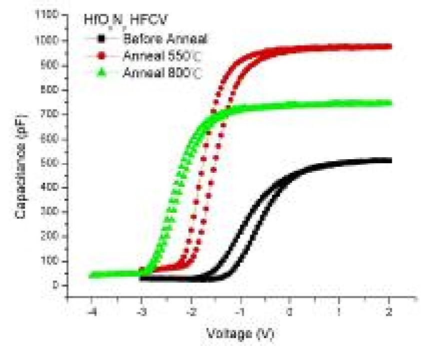
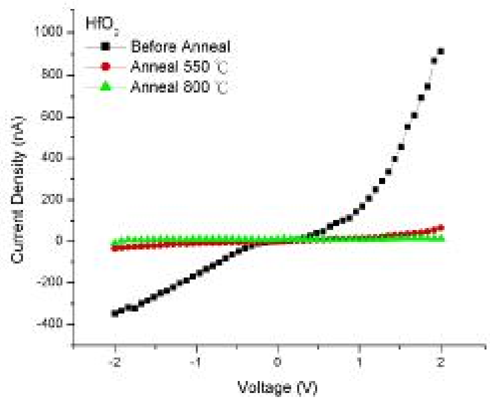


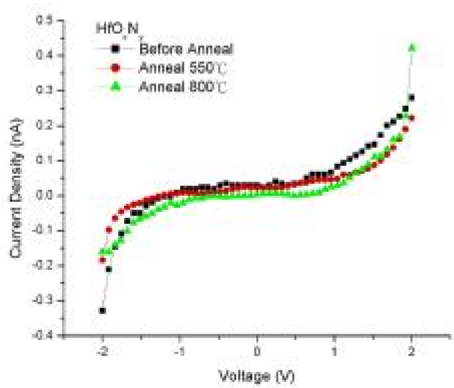
(b)

Fig.1. The measurements of C-V curves at different annealing temperatures of 500℃ and 800 ℃ as well as non-annealed samples for (a) HfO_2 and (b) HfO_xN_y.

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 HfO_xN_y films were four orders less than the HfO_2 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.



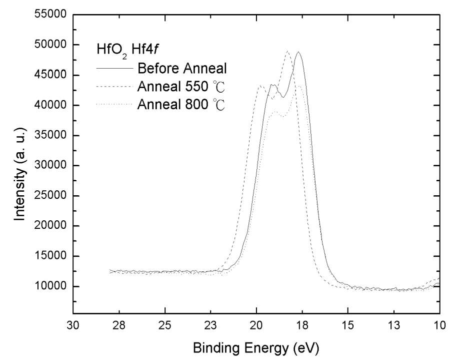
(a)



(b)

Fig. 2. The measurements of I-V curves at different annealing temperatures of 500℃ and 800 ℃ as well as non-annealed samples for (a) HfO_2 and (b) HfO_xN_y.

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_xN_y films. The depth of the O1*s* spectra are shown in Fig. 4.



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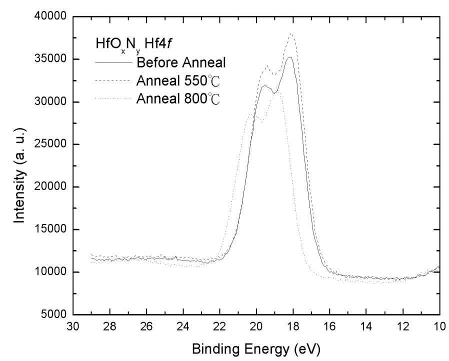
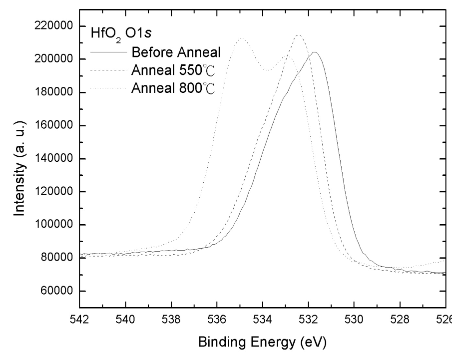


(b)

Fig. 3. Hf4*f* XPS spectra from (a) HfO_2 film. (b) HfO_xN_y film. The features' difference is due to the annealing temperature, which deposited directly on the Si substrate.

(a) and (b). In Fig. 4.(a), by increasing the annealing temperature for the HfO_2, we observe the peak of the O1*s* move to the higher binding energy, which is due to the composition transition when Oxygen moved onto the Si/high-k interface layer. Only after annealing at T = 550 ℃, the peak position shifts toward the binding energy of 532 eV, that is attributed to the silicate bonding rather than the metal-oxide bonding at the binding energy of 530 eV. It idcates 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 ℃, 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 ℃ will reduce the thermal stability. Compared with the Fig. 4.(b), we could find that the peak move in the positive direction (toward right the figure) of binding energy for the HfO_xN_y films, which explain that the bonding of the silicate layer is Si-Hf-O-N. The incorparation 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 Si2*p* spectra for analyzing the the chemical composition of the HfO_2 and HfN_xO_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



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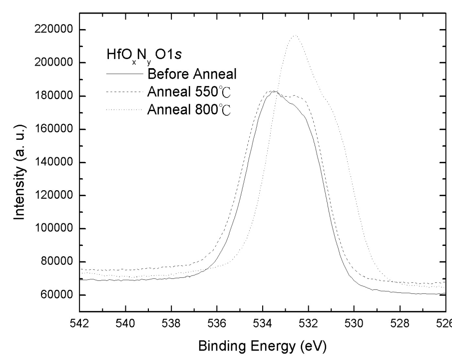


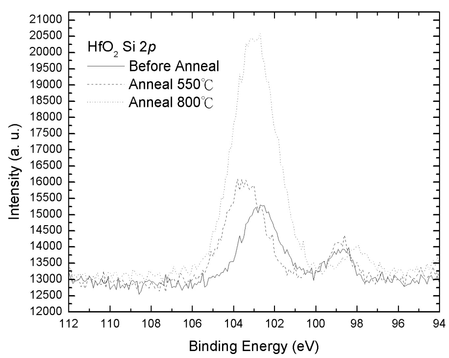
(b)

Fig. 4. XPS spectra of O1*s* for (a) HfO_2 films (b) HfO_xN_y films when annealing at different temperatures.

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 ℃. The results also confirm the importance of nitrogen, which will enhance the charge retention, decrease the EOT in conjuction with the silicon atoms, and also upgrate the thermal stability and electrical characteristics.

The EOT and optical thickness of

HfO_2 and HfO_xN_y films were shown in Fig. 6 (a) and 6 (b), respectively. The HfO_xN_y films were more stable than HfO_2, which was due to fact that the nitrogen incorporate with HfO_xN_y. Furthermore, the HfO_xN_y could not effectively increase the EOT at high annealing temperature. It is found that HfO_xN_y films have good thermal stability.



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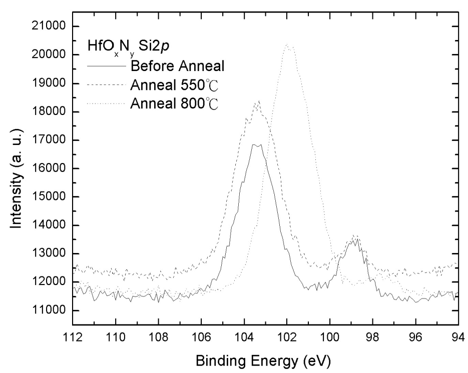
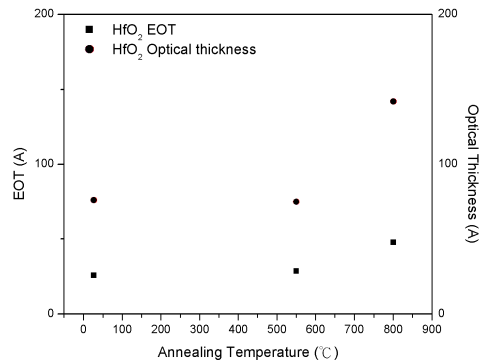


(b)

Fig. 5. Si2*p* XPS spectra for (a) HfO_2 films; (b) HfO_xN_y films, and which are annealed in forming gas at temperature of 550 ℃, and 800 ℃ for 30 min.



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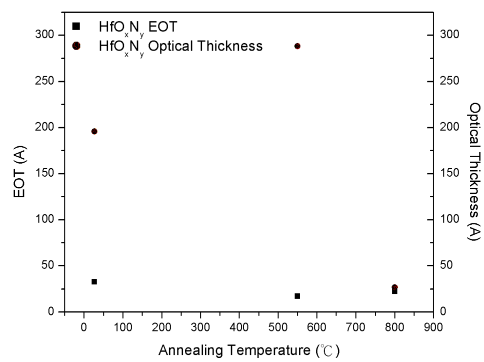

(b)

Fig. 6. The EOT and Optical Thickness (a) HfO_2 films (b) HfO_xN_y films, which are annealed at temperatures of 550 ℃ and 800 ℃ for 30 min.

4. Conclusion

In this paper, we investigated the HfO_xN_y and HfO_2 films prepared by sputtering. Compared with the HfO_2 films, the HfO_xN_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_xN_y films. By XPS analysis, we were able to confirm the nitrogen incorporation in HfO_xN_y and the formation of interfacial SiO_xN_y, where the Si-N bonding was confirmed at a annealing temperature of 800 ℃. Furthermore, the HfO_xN_y could not effectively increase the EOT at high annealing temperature.

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