Effects and mechanisms of nitrogen incorporation into hafnium oxide by plasma immersion implantation

Hei Wong, a) Banani Sen, and B. L. Yang
Department of Electronic Engineering, City University of Hong Kong, Tat Chee Avenue, Hong Kong

A. P. Huang and P. K. Chu
Department of Applied Physics, City University of Hong Kong, Tat Chee Avenue, Hong Kong

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The physics and effects of nitrogen incorporation into HfO2 films were studied in detail. The authors found that only a trace amount (~5%) of nitrogen can be introduced into the HfO2 films using plasma immersion ion-implantation technique, regardless of implantation dose. They proposed that the nitrogen incorporation is due to the filling of O vacancies (V_O) and replacement of V_O O neighbors in the bulk with nitrogen atoms. At the interface, the nitrogen atoms exist in the form of Hf–N and Si–N bonding, which significantly improve the interface properties of the HfO2/Si structure.

Temperature-dependent capacitance-voltage characteristics measurements indicate that both interface and oxide trap densities were greatly reduced with the incorporation of trace amount of nitrogen atoms. © 2007 American Vacuum Society. [DOI: 10.1116/1.2799969]

I. INTRODUCTION

Silicon dioxide (SiO2) has served as a perfect gate dielectric for over four decades and has now reached its structural limit.1–3 Searching for a physically thicker alternative high-κ dielectric material has been one of the most urgent tasks for the emerging nanoscale complementary metal-oxide-semiconductor (MOS) technology. Hafnium oxide/silicates have been considered as the most promising candidates.3–8 However, those dielectric films were still found to be thermally unstable, to have poor interface with Si, high oxide trap density and interface trap density, and a large leakage current.2 Those problems are mainly associated with the fundamental properties of the transition metal (TM) oxides. The highly electronegative nature of the d-state electrons in TM makes their oxides easy to crystallize and provide them with a large amount of oxygen vacancies and a high bulk oxide trap density.2

Several attempts for improving the dielectric properties have been made.9–17 Yet the most successful attempt is the incorporation of nitrogen atoms into the hafnium oxide. Significant improvements in both materials and electrical properties were found by introducing some nitrogen atoms into the oxide.10–17 Nitrogen was introduced into silicon oxide to improve the electrical properties of the dielectric film. There are some improvements, such as better resistance to boron diffusion and better hot-carrier reliability.2,18 However, the major electrical properties, such as the interface trap density, channel mobility, were deteriorated with the thermal nitridation. It was found that the nitrogen incorporation mainly occurred on the surface and at the SiO2/Si interface. This phenomenon was attributed to nitridation of Si–Si and silicon dangling bonds.19 In HfO2, the improvements in the material and electrical properties after the nitrogen incorporation are overwhelming. The nitrogen incorporation can increase the crystallization temperature and the dielectric constant remarkably. It also suppresses the boron penetration as similar to the oxynitride case.2,18

Both the interface and bulk properties are improved with nitrogen incorporation regardless that hafnium nitride is, in fact, a conductor. That is significantly different to the effects of silicon oxide nitridation. It was reported that the leakage current can be reduced with nitrogen incorporation into HfO2.19,20 The reduction in the leakage current was attributed to the suppression of oxygen vacancy (V_O) centers which is considered as the major conduction pathway in HfO2. Theoretical calculations have shown that the incorporation of nitrogen atoms next to the O vacancy can push the vacancy level up out of the gap.21,22 The underlying physics for the leakage current reduction is clearer now with the aid of quantum chemistry calculations. However, very little is known about the role of nitrogen at the dielectric/silicon interface and the mechanism of nitrogen incorporation although some preliminary results have been reported recently.17 A better understanding on the nature of the nitrogen incorporation and the effects of nitrogen bonds in the electrical properties improvement will help in the process optimization and for further enhancement of the device characteristics.

This work reports the physical regimes and characteristic improvement of HfO2 being implanted with nitrogen atoms. The experimental details will be given in next section. We shall introduce nitrogen atoms to the as-deposited hafnium oxide using plasma immersion ion implantation (PIII) which has advantage of low implantation energy and shallow penetration depth.12 We shall present detailed analysis of x-ray photoelectron spectroscopy measurement by using Gaussian deconvolution technique to reveal the complicated bonding structures. We shall focus on the nitrogen bonding structure in the bulk and at the dielectric/silicon interface. We shall conduct capacitance-voltage measurement at ambient temperature ranging from 100 to 400 K to probe the electron trapping characteristics.

a)Electronic mail: eehwong@cityu.edu.hk
II. EXPERIMENTS

The starting material for the metal-insulator-semiconductor capacitor fabrication is (100) n-type Si substrate with a resistivity in the range of 5–10 Ω cm. Hafnium oxide films of about 10 nm thick were deposited using an ARC-12M sputter followed by postdeposition annealing in N₂ or O₂ ambience at different temperatures for different durations.⁶⁻⁷ PIII was then conducted to introduce nitrogen atoms.¹² After several attempts with different implantation energies and doses, the implantation energy of 2 kV was chosen and the dose was 6 × 10¹⁴ or 1 × 10¹⁵/cm² for the present films; lower energy implantation would give rise to the accumulation of nitrogen atoms on the surface only, whereas larger energy PIII would cause the nitrogen atoms being penetrated into the substrate. After the nitrogen implantation (N-PIII), some samples were annealed in N₂ ambient for 15–90 min at 600 or 700 °C and some were followed with rapid thermal annealing (RTA) at 800 °C for 1 min.

To study the chemical composition and the physical structure of the films, x-ray photoelectron spectroscopy (XPS) measurements were carried out using Physical Electronics PHI 5600 with a monochromatic Al Kα x-ray source to probe the concentration profile and bonding features. The excitation energy was 1486.6 eV and the sputtering rate was about 3.2 nm/min. Since artifacts may be generated because of the effects of recombination or redistribution of ionized atoms generated during the depth profiling, nondestructive angle-resolved XPS measurements were further conducted near the dielectric/Si interface. Results showed that the main features of Si 2p and Hf 4f spectra at the interface have no major difference from both sources. For electrical measurements, a 600 nm thick aluminum layer was deposited and patterned using photolithography technique and a number of MOS capacitors in different sizes were formed. High-frequency (1 MHz) capacitance-voltage (CV) measurements using a Keithley 590 CV analyzer were conducted at ambient temperatures ranging from 100 to 400 K to probe the trapping characteristics of the dielectric films. All electrical measurements were conducted in a shielded, dark chamber at low pressure (8 × 10⁻² Torr) to avoid any electromagnetic interference, light illumination, and moisture effects.

III. RESULTS AND DISCUSSION

The amount of nitrogen (N) incorporation is very low. The concentration profiles explored using XPS measurements were depicted in Fig. 1. The largest amount of N incorporation into the film is about 5 at. % only. The nitrogen concentration did not have significant increase even rising the N-PIII dose from 6 × 10¹⁴ to 10¹⁶/cm². XPS results further indicate that the nitrogen atoms exist in the form of Hf–N bonding and have N 1s peak energy at around 396.8 eV.¹⁷ Similar phenomenon was also found in the sample prepared by the reactive sputtering deposition of HfN followed by oxidation.¹⁵ The low nitrogen content of HfO₂N₂ structure can be explained as follows. As the Hf–O bond is stronger than the Hf–N bond, very few replacements of O with N occur.¹⁷ The O content in the bulk may be reduced by about 3 at. % after the N-PIII. This phenomenon is quite similar to the case of N₂O or NH₃ nitridation of SiO₂.¹⁸ The nitrogen incorporation is limited to about 4% on the surface and at the SiO₂/Si interface.¹⁸ In the bulk the N concentration is even much lower. The N incorporation was believed due to the reaction of N with Si–Si bond or Pb centers.¹⁸ However, in the HfO₂ case, the N incorporation, even if low, is quite uniform. This observation can be attributed to the uniform distribution of O vacancies (V₀) in the samples.⁶ Because the oxidizing rate for Hf is much faster, the resultant HfO₂ are often found to have higher degree of O deficiencies.⁷ Theoretical calculation had demonstrated that incorporation of N atoms to the V₀ nearby O sites is more favorable because of the energy gain in Coulomb interaction.²¹ Considering that the reduction of O atoms in HfO₂ is less than the amount of N incorporation, we suggest that the N incorporation should take place via both the filling of O vacancies in the HfO₂ network and replacing some of the nearest neighbor O sites to V₀.

At the dielectric/Si interface, the incorporation of nitrogen also helps us to suppress the formation of Hf-silicide bonds. Figure 2(a) shows a typical Hf 4f XPS spectrum near the
interface. To have a better insight on the bonding structure, the XPS spectra were decomposed using Gaussian deconvolution. The experimental data are depicted in dots and the Gaussian deconvolution results are plotted in various line types. The existence of Hf–Si bond was evidenced with the spin-orbit splitting Hf 4f\(^{7/2}\) and Hf 4f\(^{5/2}\) at energies of about 14.5 and 16.4 eV, respectively. With N-PIII, the peak of Hf-silicide bond reduces. The Hf 4f first two doublets shift to higher energy side to about 15 and 16.7 eV, which is an indication of forming Hf–N bond.

However, we do not find any features related to the metallic Hf\(_3\)N\(_4\) bonding in those samples. With 800 °C RTA for 1 min, there is not much difference between the low-dose (6 \times 10^{14}/cm\(^2\)) and high-dose (10^{16}/cm\(^2\)) N-PIII samples. However, for high-dose sample with low temperature (600 °C) annealing [see Fig. 2(d)], a notable peak at 20 eV was found. This peak is due to O 2s of interstitial O atoms. It indicates that the high-dose implantation has resulted in the displacement of some oxygen atoms (mostly from the V\(_O\) neighbors) from the HfO\(_2\) network and forming interstitial oxygen. This peak was not found in sample with 800 °C RTA as the PIII-induced interstitial oxygen atoms might have diffused out or been consumed in the interface oxidation.

Figure 3 depicts the Hf 4f XPS spectra taken at the bulk of the sample without N-PIII and being implanted with nitrogen at dose level of 6 \times 10^{14}/cm\(^2\). In as-deposited sample [Fig. 3(a)] the predominating peaks are attributed to Hf–O bonding with Hf 4f\(^{7/2}\) (~17 eV) and Hf 4f\(^{5/2}\) (~18.5 eV). In the sample with nitrogen implantation [see Fig. 3(b)], a notable (~0.5 eV) high-energy shifts for both peaks were recorded. The double peaks with binding energies of 15 and 16.7 eV in the nitrogen implantation sample are believed to

FIG. 2. Hf 4f spectra near interface for various samples. (a) Sample without nitrogen implantation; (b) sample with N-PIII dose of 6 \times 10^{14}/cm\(^2\) and annealed at 800 °C for 1 min; (c) sample with dose of 10^{16}/cm\(^2\) and 1 min RTA at 800 °C; (d) sample with dose of 10^{16}/cm\(^2\) and furnace annealed at 600 °C for 30 min.

FIG. 3. Gaussian deconvolution of Hf 4f core level x-ray photoemission spectra in the bulk of (a) sample without nitrogen implantation and (b) sample with nitrogen implantation with dose of 10^{16}/cm\(^2\) and rapid thermal annealing at 800 °C for 1 min.
be due to the Hf–N bonding. It is noted that the Hf–N bonding is fourfold coordination which will help us to reduce the average atomic coordination number and then the defect level in the HfO$_x$N$_y$. Hafnium nitride was considered as conductive. But HfSiON with nitrogen content less than 35 at. % still demonstrates good insulating properties. Reflection electron energy loss spectroscopy measurement shows that the increases of the nitrogen content would cause the band gap energy to decrease. Hf–N bond is less ionic than Hf–O bond and gives rise to smaller band gap. However, the band gap narrowing is minimal for nitrogen content less than 10 at. %.

Figure 4 depicts the O 1$s$ spectra at interface for sample with RTA at 800 °C for 1 min. It is obvious that there exist two forms of O bonding for both low-dose and high-dose N-PIII samples. The predominate peak with energy of 532 eV is due to the O atom in the hafnium silicate. The small peak with energy of 533.5 eV is due to the Si–O bonding. No N–O bonds can be found in both N 1$s$ and O 1$s$ spectra. Similar result is also found in a sample with furnace annealing at 600 °C. The existence of Si–O bonding is further confirmed with the Si 2$p$ spectra taken at the interface, as depicted in Fig. 5. With Gaussian deconvolution, two Si 2$p$ peaks were found for the sample without N-PIII [see Fig. 5(a)] and three Si 2$p$ peaks were found for samples with N-PIII. The peaks at energies of about 98.5 and 103.62 eV in Fig. 5(b) are due to bulk Si 2$p_{3/2}$ and Si–O bonding, respectively. The peak shift can be explained as follow. The Si–O bonding energy in Hf silicate is slightly smaller than that in SiO$_2$ because of the appearance of Hf second nearest neighbor. Hf atom has more electron donating nature and transfers more charge to O atom, which in term increases the electron density on Si. As a result, the Si 2$p$ binding energy de-

![Figure 4](image1.png)

**Fig. 4.** Gaussian deconvolution of the interface O 1$s$ indicating two kinds of O bonding in the interfacial hafnium silicate layer. (a) Sample implanted with nitrogen dose of $6 \times 10^{14}$/cm$^2$ and (b) sample implanted with nitrogen dose of $10^{15}$/cm$^2$.

![Figure 5](image2.png)

**Fig. 5.** Gaussian deconvolution of Si 2$p$ at dielectric/Si interface reveals that there are three kinds of Si bonding at the interface. (a) Sample without nitrogen implantation; (b) sample with dose of $10^{15}$/cm$^2$; (c) sample with dose of $6 \times 10^{14}$/cm$^2$ and furnace annealed at 600 °C for 30 min; (d) sample with dose of $6 \times 10^{14}$/cm$^2$ and 1 min RTA at 800 °C.
increases. The middle peak in Fig. 5(b) at energy 100.6 eV corresponds to the silicide (Hf–Si) bonding. It suggested that the temperature (600 °C) of this annealing is not higher enough to nitridate the silicide bonds. For a sample with RTA annealing at 800 °C [see Figs. 5(c) and 5(d)], both the second and third peaks shift to higher energy side to 101.6 and 104.0 eV, respectively. The observation of 104.0 eV Si 2p is an indication of the interface oxidation and forming thicker SiO₂ layer. The effect of second nearest neighbor (Hf) on Si bonding is reduced. The 101.6 eV corresponds to the Si–N bonding. That is, the high temperature annealing has converted the Hf–Si bonds into Si–N bonds. In addition, the clear separated 101.6 and 104.0 eV peaks indicated that the Si–N and Si–O phases are separated at the dielectric/Si interface.²,¹⁸ The nitrogen incorporation should greatly involve the nitridation of silicide and Si–Si bonds at the interface. This reaction will help us to reduce the interface trap level to much lower value when compared to primitive HfO₂/Si interface, but should still have significant trap level than silicon oxide and silicon oxynitride because of the existence of higher-constrained Si–N phases.²,¹⁸

The small amount of nitrogen incorporation still has significant reduction on both interface and bulk trap densities. To study the trapping characteristics, high-frequency (1 MHz) capacitance-voltage (CV) measurements were conducted at different ambient temperatures. Figure 6 plots the CV characteristics for the as-deposited samples and samples with nitrogen implantation. For samples without N-PIII, large shift of the CV curves was found and there is a gradual transition between the depletion and accumulation regions. There results indicate that the bulk trap and interface trap densities are very high. The large bulk trap density was attributed to the O vacancies (V₀ centers) and grain boundary states.² As-deposited hafnium oxide was often oxygen deficient, the O vacancies in HfO₂ are electron traps, and the energy level is about 0.3 eV in the Si band gap. In HfO₂Nₓ, the V₀ level is reduced to about 0.2 eV as results of nitrogen induced band gap and valence band lowering.²⁵,²⁶ Thus the N incorporation may help us to suppress the leakage current only when the nitrogen atoms involve in either the filling of V₀ centers or the replacement V₀ neighbor O atoms such that neutral V₀ is converted into positively charged V₀. The two electrons trapped at the V₀ level are transferred to N 2p orbitals at the top of the valence band, and the V₀ related gap state disappears.²⁶

Meanwhile, the HfO₂ is also a poor glass former and can be easily crystallized at temperature as low as 325 °C. The grain boundary states at microcrystallite surface have quite shallow energy levels and may not be able to trap electron at room temperature. It participates in the current conduction and can be filled with electron at lower temperatures. The large positive shift of the CV curve measured at 250 K can be explained with the shallow trap effect. With nitrogen implantation, as shown in Fig. 6, the sample has pronounced reduction in flatband shift of temperature-dependent CV characteristics. The amount of bulk traps has been significantly suppressed. In addition, the N-implanted sample has much steeper slope in the transition region of the CV curves. It indicated that the interface trap density has been reduced to a very low level.

The bulk trap removal is mostly due to the removal of V₀ centers with nitrogen incorporation. The significant reduction on the interface trap should be due to the combined effect of several improvements occurred at the interface. The HfO₂/Si interface can be either O or Hf terminated; the existent of Hf–Si bonds is one of the major sources for interface traps.² The Hf–Si bonds are amphoteric centers and have an energy level lie in the Si band gap. As revealed with XPS in a previous section, a large amount of Hf–Si bonds was found at the HfO₂/Si interface. With nitrogen implantation, the Hf–Si bonds can be converted into a Hf–N bond. Unlike the O atom in HfO₂ which is sixfold coordinated, the N atom in HfO₂ is fourfold coordinated; this will help us to reduce the average coordination number at the interface and a better interface is expected.² Another cause for the interface improvement is due to the forming SiO₂ layer. The trace amount of oxygen released from the nitrogen substitution can react with the substrate Si at 800 °C post-implant annealing. Finally, although separated Si–N phases, which can deteriorate the SiO₂/Si interface, were also formed; they still contributed to the interface improvement as Si–N bonding is still better than the Hf–O and Hf–Si bonding at the interface.

IV. CONCLUSIONS

The physics and effects of nitrogen incorporation into the HfO₂ were studied. Only a trace amount (~5%) of nitrogen can be introduced into HfO₂ by plasma immersion ion-implantation technique, regardless of implantation dose. The nitrogen incorporation is believed to take place via the following mechanisms: (a) filling of the O vacancies (V₀) in the bulk of HfO₂, (b) replacement of O atoms of the V₀ neighbors which will make the V₀ centers inactive, (c) nitridation of the interfacial Hf–Si bonds, and (d) nitridation of the interfacial Si–Si bonds and substrate Si.
Hence, although the amount of nitrogen incorporation is low, significant improvements on both the material and the electrical properties are still recorded as the nitrogen incorporation mainly involved the defect centers. Electrical measurements indicate that both interface and oxide trap densities are greatly reduced as results of the removal of interfacial silicade bonds, removal of the $V_O$ centers, or making the $V_O$ centers inactive in the bulk.

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