Nitrogen Incorporation into Hafnium Oxide Films by Plasma Immersion Ion Implantation

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(Received November 16, 2006; accepted February 19, 2007; published online May 17, 2007)

The physics and effects of nitrogen incorporation into hafnium oxide (HfO$_2$) films were studied in detail. We found that only a trace amount ($\sim$5%) of nitrogen can be introduced into the HfO$_2$ films by plasma immersion ion-implantation, regardless of implantation dose. We proposed that the nitrogen incorporation is mainly due to the filling of O vacancies in the as-deposited HfO$_2$ films and the nitridation of silicide bonds at the HfO$_2$/Si interface. Temperature-dependent capacitance–voltage and current–voltage characteristics measurements indicate that both interface and oxide trap densities were greatly reduced as the results of the nitrogen filling of the O-vacancies and the nitridation of interfacial hafnium silicide bonds.

[DOI: 10.1143/JJAP.46.3234]

KEYWORDS: nitrogen, hafnium oxide, X-ray photoelectron spectroscopy, oxygen vacancy

1. Introduction

The revolutionary progress in silicon microelectronics is one of the premium pillars for today’s technological achievements in every aspect. This is accompanied by the downsizing of metal–oxide–semiconductor (MOS) transistors.1,2 Today, we reach the verge of technological and structural limits of SiO$_2$. This signifies the need for a perfect gate dielectric for several decades.3,4 If MOS structures are still to be used in future technology nodes, obtaining a physically thicker high-κ dielectric material to replace a conventional oxide and preserving the capacitance are indispensable. A good candidate for replacing SiO$_2$, in addition to a high-κ value, should satisfy several other requirements.2,3 Among transition metal (TM) oxides, hafnium oxide (HfO$_2$) has drawn considerable attention in this respect, owing to its several promising characteristics.5–8 HfO$_2$ is still found to be thermally unstable and to have low-quality interface with Si, a high oxide trap density, a high interface trap density, and a large leakage current.2 These problems are mainly due to the fundamental properties of the TM oxides. The highly electronegative nature of the d-state electrons in the TM makes their oxides easy to crystallize and provide them with a large number of oxygen vacancies and a high bulk oxide trap density.2,8 It has recently been found that adding N to an oxide could markedly improve the characteristics.9–15

In this paper, we report the physical regimes, characteristic improvements and effects of thermal annealing of HfO$_2$ implanted with nitrogen atoms. Experimental details will be given in the next section. Nitrogen atoms were introduced into an as-deposited hafnium oxide by plasma immersion ion implantation. This method has advantages, such as a low implantation energy and a small penetration depth. As the small physical thickness of the dielectric is required, other implantation techniques are not appropriate as the implant is difficult to control and easily penetrates the substrate. Other nitridation techniques, such as plasma nitridation are expected to result in a nonuniform nitrogen distribution, Capacitance–voltage and current–voltage measurements, at ambient temperatures ranging from 100 to 400 K, have been conducted. Such techniques enable the probing of the electron trapping characteristics at different energy levels. In addition to the electrical results, the results of the detailed analysis of X-ray photoelectron spectroscopy (XPS) measurements using a Gaussian deconvolution technique to reveal complex bonding structures are presented. The focus is on the nitrogen bonding in the bulk and at the dielectric/silicon interface.

2. Experimental Procedure

HfO$_2$ films of about 10 nm thick were deposited by ARC-12M sputtering and subsequent post-deposition annealing in N$_2$ or O$_2$ ambient at different temperatures for different durations was performed.6,7 Plasma immersion ion-implantation (PII) was then conducted to introduce nitrogen atoms.9 The implantation energy was 2 kV and the dose was $6 \times 10^{14}$ or $1 \times 10^{16}$/cm$^2$. After the nitrogen PII (N-PII), some samples were annealed in N$_2$ ambient for 15 to 90 min at 600 or 700°C and some were treated by rapid thermal annealing (RTA) at 800°C for 1 min.

To study the chemical composition and physical structure of the dielectric films, XPS measurements were carried out using Physical Electronics PHI 5600 with a monochromatic Al Kα X-ray source to probe the 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 XPS16 measurements were further conducted near the dielectric/Si interface. The obtained results showed that the main features of the 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 by a photolithography technique and a number of MOS capacitors in different sizes were formed. Current–voltage (I–V) measurements using Keithley 236 Source Measure Units and high-frequency (1 MHz) capacitance–voltage (C–V) 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 a low pressure (8 × 10⁻² Torr) to avoid any electromagnetic interference, light illumination and moisture effects.

3. Results and Discussion

The amount of nitrogen incorporation is very low. The typical concentration profile explored by XPS measurements is shown in Fig. 1. The amount of N incorporated into the film is about 5% for nitrogen plasma implantation at a dose of 6 × 10¹⁴ or 10¹⁶/cm². Figure 2 shows some typical N 1s XPS spectra of the HfO₂ sample being implanted with nitrogen. A weak peak appears at around 396.8 eV, corresponding to the Hf–N bond throughout the film. A similar phenomenon was found in sample prepared by the reactive sputtering deposition of HfN followed by oxidation.¹¹ The low nitrogen content of the HfOₓNᵧ structure can be explained by the occurrence of very few replacements of O by N, as the Hf–O bond is stronger than the Hf–N bond. Replacement may still occur in some disordered sites, such as the neighbors of oxygen vacancies. This phenomenon is similar to the case of N₂O or NH₃ nitridation of SiO₂.¹⁴,¹⁵ The nitrogen incorporation is limited to about 4% on the surface and at the SiO₂/Si interface.¹⁵ In the bulk, the N concentration is even much lower. The N incorporation was believed to be due to the reaction of N with Si–Si bonds or Pᵦ₀ centers.¹⁵ However, in the HfO₂ case, the N incorporation, even if low, is uniform (Figs. 1 and 2). This observation can be attributed to the uniform distribution of O vacancies (Vₒ) in the sample.⁶ As the oxidation rate of Hf is high, the resultant HfO₂ films are often found to have a high degree of O deficiency.⁻² The N incorporation occurs mainly owing to the filling of O vacancies with nitrogen in the HfO₂ network. At the interface, the incorporation of nitrogen also helps in suppressing the formation of Hf–silicide bonds. Figure 3 shows the typical Hf 4f XPS spectra at different locations on a sample. The peak intensity of the Hf–silicide bond decreases and shifts to the high-energy side, indicating the formation of Hf–N bonds. To have a better insight on the bonding structure of the incorporated nitrogen atoms, we conducted a detailed analysis of the
Hf 4f, Si 2p, and O 1s XPS spectra by using the Gaussian deconvolution technique. Figure 4 shows the Hf 4f XPS spectra obtained in the bulk of the sample implanted with nitrogen at a dose level of 10^{16}/cm^2. The experimental data are plotted in dots and the Gaussian deconvolution results are represented with various line types. The predominant peaks are attributed to Hf–O bonding with Hf 4f_{7/2} (~18 eV) and Hf 4f_{5/2} (~20 eV). Compared with the samples without nitrogen implantation, notable (~0.5 eV) high-energy shifts for both peaks are recorded. The double peak with binding energy of 15 and 16.7 eV are believed to be due to the Hf–N bonding. Although the double peak feature of the Hf–Si bond has a similar energy range (14.3 and 16.2 eV), the low Si content in the bulk and the strong Hf 4f_{5/2} peak at 16.7 eV suggest that this feature should be due to the Hf–N bonds. It should be noted that the Hf–N bonding is fourfold coordinated, which aids in reducing the average atomic coordination number and thus the defect level in HfO_2. It is noted that the sample subjected to 600°C annealing exhibits a peak with an energy of about 21 eV. The peak is attributed to O 2s. This suggests that N-PII results in some oxygen displacements. The oxygen sites near the O vacancies can be replaced with nitrogen atoms from the

energy point of view. The released oxygen atoms become interstitial oxygen and exhibit the O 2s spectrum. At 800°C RTA, the interstitial oxygen diffuses to the interface and is involved in the oxidation of interfacial Si–Hf bonds and the substrate Si; no O 2s peak can be detected.

Figure 5 shows the O 1s spectra at the interface for the sample prepared by RTA at 800°C for 1 min. It is obvious that there exist two types of O bonding. The predominant peak with the energy of 532 eV is due to the O atom in the hafnium silicate. The small peak with the energy of 533.5 eV is due to the Si–O bonding. A similar result is also found in the sample prepared by furnace annealing at 600°C. The existence of Si–O bonding is further confirmed using the Si 2p spectra taken at the interface, as depicted in Fig. 6. Three Si 2p peaks are observed by Gaussian deconvolution. The peaks at the energies of about 98.5 and 103.62 eV are due to the bulk Si 2p. The peak with the energy of 101.6 eV corresponds to the Si–N bonding, indicating that the Hf–Si bonds are converted into Si–N bonds by high-temperature annealing. In addition, the Si–N phases are separated at the dielectric/Si interface. The nitrogen incorporation should be greatly involved in the nitridation of silicide and Si–N phases at the interface instead of replacing the oxygen bonds. This reaction would aid in reducing the interface trap level to a much lower value than that for the primitive HfO_2/Si interface; however, it should still have a significantly higher trap level than the silicon oxide and silicon oxynitride because of the existence of highly-constrained Si–N phases.

Although the amount of nitrogen incorporation is small, it still induces significant improvements in the material and electrical properties. Figure 7 shows the temperature-dependent C–V characteristics of HfO_2 samples with and without nitrogen implantation. The larger shift of the C–V curves and the smooth transition between the depletion and
accumulation regions of the samples without N-PIII indicating the bulk trap and interface trap densities are very high. The large bulk trap density is attributed to the O-vacancies (\(V_O\) centers) and the grain boundary states. The nitrogen-implanted sample has pronounced reductions in both bulk trap and interface trap levels in a wide energy range, as evidenced by the small flatband shift and steep slope in the transition region of the \(C-V\) curves. The bulk trap removal is mostly due to the removal of \(V_O\) centers with nitrogen incorporation. The significant reduction in the interface trap density should be due to the combined effect of several improvements at the interface. As revealed by XPS in the previous section, a large amount of Hf–Si bonds are found at the HfO\(_2\)/Si interface. With nitrogen implantation, Hf–Si bonds can be converted into Hf–N bond. This aids in reducing the average coordination number at the interface and a better interface is expected. The interface improvement is also due to the formation of the SiO\(_2\) layer. The trace amount of oxygen released from the nitrogen substitution can react with the substrate Si at 800 °C post-implantation annealing. Figure 8 shows the trap activation energies extracted from the temperature-dependent \(I-V\) curves at different electric fields. Two major traps are still present in the N-PIII sample but their concentrations are been greatly reduced. The observed trap at \(E_{act}\) of about 12 meV is ascribed as a shallow one. Shallow trap is proposed as one of the major causes of the large leakage current in hafnium

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**Fig. 6.** The Gaussian deconvolution of the Si 2p at dielectric/Si interface reveals the presence of three kinds of Si bonding at the interface. (a) Sample prepared by furnace annealing at 600 °C for 30 min; and (b) sample prepared by rapid thermal annealing at 800 °C for 1 min. The nitrogen dose for plasma immersion ion implantation was \(10^{16}\)/cm\(^2\).

**Fig. 7.** \(C-V\) characteristics of hafnium oxide (upper diagram) and hafnium oxide with nitrogen implantation (lower diagram).

**Fig. 8.** Trap energies extracted from \(I-V\) characteristics measured at several different temperatures.
oxide and the trap at $E_{ac2}$ of about 0.364 eV should be due to $V_O$ centers. It should be noted that there are some discrepancies in the data obtained at different electric fields. The leakage current characteristics of high-$\kappa$ metal oxides are very complex and there is no unified model available so far. Several factors would affect the accuracy of determining the activation energy. First, for the sake of simplicity, the electric field is estimated from the applied voltage only. The surface potential of silicon is not taken into account. On the other hand, since the trap energy levels are estimated from the current density, the major source of the discrepancies should be the current components due to the absence of trap-assisted charge transportation. Nevertheless, the 0.364 eV trap seems less sensitive to the actual electric field and the disturbance of other charge transport mechanisms.

4. Conclusions

The physics and effects of nitrogen incorporation into HfO$_2$ were studied. Only a trace amount (~5%) of nitrogen can be introduced into HfO$_2$ by plasma immersion ion-implantation, regardless of implantation dose. The nitrogen incorporation is believed to be induced mainly by filling the O vacancies in HfO$_2$ and by nitridating the silicide bonds at the HfO$_2$/Si interface. Despite the fact that the amount of nitrogen incorporation is low, significant improvements in both the material and electrical properties are recorded. Electrical measurements indicate that both interface and oxide trap densities are greatly reduced by the removal of O-vacancies and silicide bonds.

Acknowledgment

This work was supported by a UGC Grant of Hong Kong (Project No. CityU 1167/03E).