Electrical properties of HfO$_x$N$_y$ thin films deposited by PECVD


Department of Chemistry and Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon 440-746, South Korea

Available online 17 August 2006

Abstract

In this study, we deposited the hafnium oxy-nitride (HfO$_x$N$_y$) film because it shows significant reduction in leakage current density and superior thermal and electrical stability and it also exhibits the increase in crystallization temperature depending on the nitrogen concentration. HfO$_x$N$_y$ thin films were deposited in the temperature at 500 °C on p-type Si (100) substrates by plasma enhanced chemical vapor deposition method, using hafnium tert-butoxide (Hf(OtBu)$_4$) as the hafnium oxide precursor. A mixture of NH$_3$ (60%) and N$_2$ (40%) in volume ratio was used as the reactive gas. In addition, we have also investigated the relationship between leakage currents and structures of the coating layers by the effects of composition and annealing temperature.

© 2006 Elsevier B.V. All rights reserved.

PACS: 78.6606-w

Keywords: Thin film; High-k dielectrics; PECVD; Leakage current density; Thermal stability

1. Introduction

Among high-k gate dielectric materials, the HfO$_2$ exhibits the high dielectric constant (25–30) [1], large band gap (5.68 eV), large band offset (1.5 eV), and thermodynamic stability on silicon. Several superior properties of SiO$_2$ allowed the fabrication of properly working metal-oxide-semiconductor-filed-effect-transistor (MOSFET) with 1.5 nm thickness of SiO$_2$ gate layers [2,3]. However, as argued below, further scaling of the SiO$_2$ gate layer thickness is problematic. So, various high-k materials have been studied as replacement for SiO$_2$ as a gate dielectric in metal-oxide-semiconductor (MOS) devices in recent years [4]. However, many important characteristics, which are already well known and controlled for SiO$_2$, have yet to be understood for high-k materials. Two candidates are HfO$_2$ and HfO$_x$N$_y$ due to their reasonably high dielectric constant [5], low-leakage current [6], and a relative large band gap [7]. A fundamental problem in their development, however, is crystallization after thermal treatment above 500 °C, because grain interfaces which serve as leakage current path are formed [8]. Poly-crystallization of thin film generates grain boundaries in thin dielectric film which acts as oxygen diffusion and leakage current path, resulting in high leakage current. Therefore, to remain in an amorphous state after thermal process is important to achieve the lower leakage current. Moreover, when a high-k metal oxide like HfO$_2$ is deposited on a Si substrate, an ultra-thin low-k interfacial layer, either SiO$_x$ or Si$_x$M$_y$O$_z$ (where M is Hf) forms at the silicon interface. The interfacial layer grows either during the deposition of the high-k dielectric or during post-deposition anneals processes. Therefore it is important to investigate both the crystallographic phase evolution and interfacial layer after annealing. Recently, it was reported that HfO$_x$N$_y$ formed by incorporating N into HfO$_2$ could improve the thermal stability and electrical properties of these gate dielectric films [9,10]. In this work, we studied the electric properties of HfO$_x$N$_y$ films grown by plasma enhanced chemical vapor deposition (PECVD).

2. Experimental

The procedure of HfO$_2$ and HfO$_x$N$_y$ fabrications was done in a set of PECVD system which is shown in the Fig. 1. The Radio Frequency (RF) sources with frequency 13.56 MHz were derived in the power range of 100–200 W, respectively. The plasma source gas was Ar gas with the flux of 100–150 sccm. A mixture of NH$_3$ (60%) and N$_2$ (40%) in volume ratio were used
as the reactive gas. A mixture of NH₃/N₂ gas was used in the range of 20–70 sccm flux. During deposition, the total pressure was kept constant at 300 mTorr. The substrates that were laid on a 4-inch size graphite heater were one-side polished single crystalline p-type silicon wafer with (100) crystal surface. Before they were installed on the heater in the deposition chamber, they underwent degreasing and drying in vacuum. The detailed descriptions of experimental set-up and deposition procedure have already been published elsewhere[11,12]. The HfOₓNᵧ thin films were deposited in the temperature range of 100–500 °C on substrates using hafnium tert-butoxide (Hf(O)tBu)₄) as a hafnium oxide precursor, without the carrier gas. The deposition time was in the range of 10–90 min. As-deposited samples were annealed at 600 °C to 900 °C for 20 min in O₂ ambient in the furnace. The as-grown films were analyzed with X-ray photoemission spectroscopy (XPS) as well as X-ray diffraction (XRD) technique. Physical thickness of HfOₓNᵧ thin film was measured using high-resolution transmission electron microscopy (HTEM). The capacitance-voltage (C-V) curves of the MOS capacitor were measured using a HP4194A impedance/gain-phase analyzer.

3. Results and discussion

The results of XPS analysis for the HfOₓNᵧ and HfO₂ thin films deposited at 500 °C were shown in Fig. 1. The shift of whole peak was calibrated by carbon 1s peak. In order to investigate the chemical bond shift of the interfacial layer due to annealing processes, Hf 4f½ and O 1s peaks were analyzed to confirm the deposition of HfOₓNᵧ and HfO₂. In the case of HfO₂, which use hafnium tert-butoxide (Hf(O)tBu)₄) as a precursor, deposited by Ar plasma, Hf 4f½ peak ranged from 15.9 eV to 16.4 eV after annually at 900 °C. When the HfOₓNᵧ films formed with NH₃/N₂ plasma, Hf 4f½ peak ranged from 15.6 eV to 16.1 eV as well as N1s shifted from 398.9 eV to 399.4 eV in the insert of Fig. 1b. And this result supported that the deposited film is HfOₓNᵧ, because Hf 4f½ peak of HfOₓNᵧ thin film indicated lower binding energy than that of HfO₂. Reacting hafnium metal with oxygen formed HfO₂ and this O 1s peak was located from 530.1 eV to 532.1 eV as shown in Fig. 1a. In the interfacial layer of as-deposited HfO₂ thin film, Hf concentration decreased with increasing annealing temperature. On the other hand, Si and O concentrations increased at the same control, because the interfacial layer approximated Si–Hf–O phase. But, in the HfOₓNᵧ thin film as compared with HfO₂ thin film, the Si–Hf–O concentration of the interfacial layer decreased with increasing annealing temperature. This result informed that nitrogen prevents a diffusion of oxygen during the annealing process.

Thickness was measured using cross sectional of TEM and their images are shown in Fig. 2. HfOₓNᵧ thin film measured to be 20 nm thick and HfO₂ also measured to be 20 nm thick. In the case of using NH₃/N₂ plasma as reaction gas, different to Ar plasma, interfacial layer shown a small form see Fig. 2. So, this is indicated that nitrogen blocks the oxygen diffusion to the interfacial layer as same as the result of XPS mentioned above. As shown in the Fig. 2b and d, thickness of as-deposited HfOₓNᵧ and HfO₂ samples annealed at 900 °C decreased because these thin films had high density. But the decrements of HfOₓNᵧ samples were lower than that of HfO₂ sample (see
Fig. 2d for 20 min in O2 ambient). In conclusion, at 500 °C, the NH3/N2 plasma could important role of preventing from oxygen diffusion to the SiO2 interfacial layer due to HfOxNy layer formation. Also, the HfOxNy player prohibited further SiO2 interfacial layer growth, resulting in decreasing leakage current density.

Thicker films with 50 nm thickness than those typically used as gate dielectric were used because the crystallinity of ultra-thin films cannot be defined by XRD. As-deposited thin films at 500 °C had only Si (200) peak, this indicated that the thin film wasn’t crystallized yet. But, at 700 °C under the oxygen ambient, crystalline peaks of (110), (11), (100), (002), (200), and (102) planes appeared. As shown in Fig. 3, annealed HfOxNy thin film mainly exhibited peaks of (11), (100), (002), (200), and (02) planes while HfO2 shows crystalline peaks of (110), (11), and (100) planes. Noticeable thing was that main crystalline peaks for the annealed HfO2 and HfOxNy were (11) and (002), respectively.

Fig. 4 shows C–V characteristics of Al/ HfOxNy/Si and Al/ HfO2/Si structures annealed at various furnace temperatures in O2 ambient. The Al/ HfOxNy/Si and Al/HfO2/Si structures showed clear accumulation, depletion and inversion regions. Since the thickness of HfOxNy and HfO2 thin films decreased, the capacitance of Al/HfOxNy/Si and Al/HfO2/Si structures increased with increasing annealing temperature. As shown in Fig. 4, flat band voltage shift of HfO2 capacitors annealed in O2 ambient is larger than that HfOxNy in O2 ambient. The excessive oxygen concentration in HfO2 films annealed in O2 ambient produced the effective negative charges coming from excessive oxygen interstitial defects and they increased with increasing annealing temperature, resulting in a large shift to the positive side of flatband voltage.
The leakage current characteristics of Al/HfO\textsubscript{x}N\textsubscript{y}/Si and Al/HfO\textsubscript{2}/Si structure annealed in O\textsubscript{2} ambient are shown in Fig. 5. The leakage current densities of the films increased with increasing annealing temperature in O\textsubscript{2} ambient. The leakage current densities of the HfO\textsubscript{x}N\textsubscript{y} and HfO\textsubscript{2} films at 500 °C were about $8.83 \times 10^{-10}$ and $6.1 \times 10^{-8}$ A/cm\textsuperscript{2}, respectively, at $-1$ V. Also, the leakage current densities of the HfO\textsubscript{2} annealed in O\textsubscript{2} at 900 °C is about $1.8 \times 10^{-3}$ A/cm\textsuperscript{2} at $-1$ V. However, the leakage current density of the HfO\textsubscript{x}N\textsubscript{y} heat treated in O\textsubscript{2} at 900 °C is improved, which is about $1.5 \times 10^{-6}$ A/cm\textsuperscript{2} at an applied voltage of $-1$ V.

Consequently, the leakage current increased after as-deposited thin film treated annealing (Fig. 6). This result was attributed from two main reasons. The first reason is the higher increment of leakage current for HfO\textsubscript{2} than HfO\textsubscript{x}N\textsubscript{y} was due to the increment of the crystallization of these thin films. Second reason is decrement of Si–Hf–O concentration in the interfacial layer for HfO\textsubscript{x}N\textsubscript{y} as compared to HfO\textsubscript{2} because nitrogen blocked the oxygen diffusion to this region.

4. Conclusions

Hafnium oxy-nitride thin films for gate dielectric were deposited at 500 °C on p-type Si (100) substrates by PE-MOCVD. As-deposited HfO\textsubscript{x}N\textsubscript{y} films showed an amorphous structure, but samples annealed in O\textsubscript{2} ambient at 700–900 °C showed the increase of crystallinity. The flatband voltage shifts of HfO\textsubscript{x}N\textsubscript{y} capacitors annealed in O\textsubscript{2} ambient are smaller than HfO\textsubscript{2} in O\textsubscript{2} ambient because nitrogen blocked the oxygen diffusion to the interfacial layer. Also, the leakage current densities of the HfO\textsubscript{x}N\textsubscript{y} and HfO\textsubscript{2} films annealed at 900 °C in O\textsubscript{2} were about $1.5 \times 10^{-6}$ and $1.8 \times 10^{-3}$ A/cm\textsuperscript{2}, respectively, at $-1$ V. The leakage current density of HfO\textsubscript{x}N\textsubscript{y} films is approximately three orders of magnitude lower than that of HfO\textsubscript{2} for the same capacitance equivalent oxide thickness (CET).

Acknowledgements

Support of this research by the BK 21 project of Ministry of Education, Korea is gratefully acknowledged. This work was also supported by the Center for Advanced Plasma Surface Technology in the Sungkyunkwan University.

References