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Atomic scale nitrogen depth profile control during plasma enhanced atomic layer deposition of high k dielectrics

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Nitrogen incorporation produces several benefits in the performance of high k gate oxides. However, since too much nitrogen incorporation at the interface of gate dielectric can result in device degradation, the atomic scale control of nitrogen depth profile is desirable. In this study, the authors have improved electrical properties and interface properties by depth profile control of *in situ* nitrogen incorporation during plasma enhanced atomic layer deposition. The best electrical properties in terms of hysteresis, equivalent oxide thickness, and interface states were obtained when the nitrogen is incorporated in the middle of the thin film, which has not been achievable by other techniques. © 2007 American Institute of Physics. [DOI: 10.1063/1.2776350]

The incorporation of nitrogen atoms reduces the leakage currents and improves the reliability of the metal-oxide-semiconductor field effect transistors by prohibiting boron penetration, passivating oxygen vacancy states, and enhancing structural stability.¹ Generally, the nitrogen incorporation into gate oxide has been carried out by high temperature or plasma annealing of oxide films under nitrogen environment. However, since too much incorporation of nitrogen at the interface between channel region and gate oxide induces large flatband voltage shift resulting in the mobility degradation,² postdeposition nitridation process has been suggested.^{3,4} Comparative study between samples with nitride layer located at the bottom and top of oxide has shown better electrical properties for the top nitrided samples.³ However, with further scaling of devices into nanoscale regime, a more precise control of nitrogen depth profile would be desirable.

Due to its atomic scale thickness controllability, atomic layer deposition (ALD) is an ideal technique to produce thin films with atomically modulated compositional depth profiles. However, the incorporation of elements (additives or dopants) to thin films with predesigned depth profile during ALD has not been studied yet. Recently, we reported *in situ* nitrogen incorporation into Ta₂O₅ thin films during thermal and plasma enhanced ALD (PE-ALD) by employing NH₄OH and N/O mixture plasma as a source for reactants, which resulted in significantly improved electrical properties.^{5,6} In this letter, we show that atomic scale depth profile control of nitrogen is feasible by *in situ* nitrogen incorporation during ALD. The *in situ* nitridation during PE-ALD HfO₂ was carried out by adding nitrogen to oxygen plasma. HfO_xN_y thin films with three different nitrogen depth profiles were prepared by incorporating nitrogen atoms into the bottom, middle, and top of the PE-ALD HfO₂ thin films, and the effects of *in situ* nitridation and nitrogen depth profiling on the electrical properties were comparatively studied. It should be noted that although the nitrogen incorporation into the bottom and top of oxide has been performed by other nitridation techniques,³ the nitrogen incorporation into the middle of the oxide by one simple process step has not been

reported yet. The best electrical properties were obtained for this case.

A homemade remote plasma enhanced ALD system was used in this study. Tetrakis(dimethylamino)hafnium was used as a Hf precursor with oxygen and nitrogen as reactants. For *in situ* nitridation, the N/O flow ratio was fixed at 2. The impurity contents and chemical binding structures were analyzed by angle resolved x-ray photoemission spectroscopy (AR-XPS) at 90° and 30° detection angles. For electrical measurements, metal-oxide-semiconductor (MOS) capacitors with dc sputtered Pt as electrodes were fabricated on *p*-type (boron, $5 \times 10^{14}/\text{cm}^3$) Si(001) substrates. Postdeposition annealing (PDA) and forming gas annealing were carried out at 400 °C for 10 min in oxygen environment and for 30 min in H₂ 5%–N₂ 95%, respectively. Capacitance-voltage (*C-V*) and current-voltage (*I-V*) characteristics were determined by using Keithley 4200 semiconductor parameter analyzer with HP4284 LCR meter. The equivalent oxide thickness (EOT) values were extracted from *C-V* measurements using a resistance correction procedure carried out at two different measurement frequencies of 10 and 100 kHz,⁷ and the interface state density (D_{it}) was obtained by conductance methods.

First, fully nitrided HfO_xN_y thin films were prepared in order to confirm the nitrogen incorporation through *in situ* nitridation during PE-ALD HfO₂. The growth rate remained constant by adding the nitrogen to oxygen plasma (1.3 Å/cycle) and x-ray diffraction analysis has shown that all the films are amorphous at the low growth temperature used in this study (250 °C). The nitrogen content in the film was determined to be 4.5% by XPS for fully nitrided HfO_xN_y thin film. The nitrogen incorporation during PE-ALD HfO₂ has been recently reported by using N₂O plasma as an oxidant.⁸ However, by the current process scheme using the mixture of nitrogen and oxygen gases, the nitrogen content is controlled more readily by changing the N/O flow ratio. The effects of *in situ* nitridation on electrical properties were investigated by comparing the electrical properties of MOS capacitors with PE-ALD HfO₂ and HfO_xN_y as dielectrics. The EOT value of HfO_xN_y (0.95 nm) was smaller than that of HfO₂ (1.15 nm). This agrees with a previous report showing that 5% N incorporation in HfO₂ films increases the dielectric constant by about 17%.⁹ However, the flatband volt-

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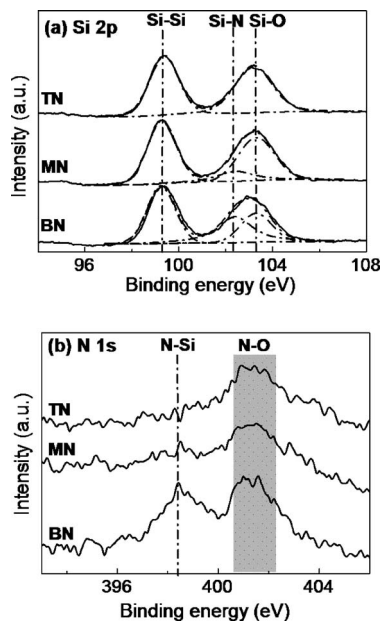


FIG. 1. (a) Si 2p and (b) N 1s XPS spectra of as-deposited BN (bottom nitridation), MN (middle nitridation), and TN (top nitridation).

age (V_{FB}) of HfO_xN_y is shifted to slightly negative direction with $\Delta V_{FB} = -0.15$ V, and the hysteresis becomes larger (about 0.2 V) compared to HfO_2 . Leakage current density of HfO_xN_y at -1 MV/cm is 1×10^{-7} A/cm², which is about ten times lower than that of HfO_2 (data not shown). These results are consistent with previous reports indicating that too much nitrogen incorporation at the interface of high k /Si causes flatband voltage shift and large hysteresis, which would lead to the degradation of device performance.¹ These results indicate that the depth profile control for nitrogen incorporation is highly desirable.

Thus, three different samples with atomically modulated nitrogen depth profiles were prepared. The positions of nitrided layers were controlled by changing the sequence of O plasma and N/O mixture plasma exposures to produce bottom nitridation (BN), middle nitridation (MN), and top nitridation (TN) samples. The total number of growth cycles was 30 for each sample, 20 cycles of O plasma and 10 cycles of N/O mixture plasma as a reactant, respectively. Figure 1(a) is the XPS spectra of these three samples in Si binding energy region, showing that each spectrum is composed of two peaks, a peak from Si-Si bonding at 99.3 eV and another peak at around 103.0 eV. While the positions of Si-Si bonding peaks from the Si substrates are all the same for three spectra, the peak positions of higher binding energy are shifted to lower energy from sample TN to BN. By deconvolution, we found that while the high energy peak for TN is composed of entirely Si-O peak at 103.3 eV, the peak for BN is actually composed of two peaks at 103.3 and 102.4 eV. The peak at 102.4 eV is attributed to the Si-N bonding.¹⁰ While the Si-N peak intensity for MN is very small, that for BN has almost same intensity as that of Si-O, revealing that significant Si-N bonds exist for BN sample. In addition, the XPS spectra of three samples in nitrogen binding energy region [Fig. 1(b)] show that while only one broad N-O bonding peak is observed at 401–402 eV¹¹ for TN sample, additional peak due to N-Si bond at 398.2 eV (Ref. 12) is observed for BN. The existence of Si-N bonds for BN indicates that nitrogen is incorporated into the bottom

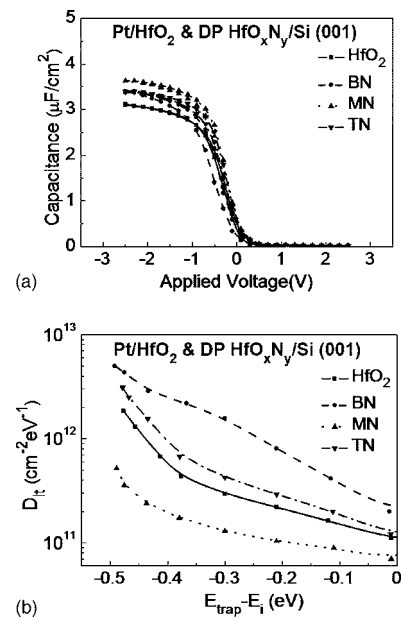


FIG. 2. (a) Capacitance-voltage curves and (b) the interface state densities of MOS capacitors with HfO_2 and DP (depth profiled controlled) HfO_xN_y as a gate insulator.

layer of HfO_2 , forming an interface layer with Si-N bonds as well as Si-O bonds. However, no Si-N bond is formed for TN since nitrogen incorporation occurs only at the top portion of the oxide, which is away from the interface region. The transmission electron microscopy analysis (data not shown) has shown that the total thickness of BN (4.5 nm) was slightly thicker than those of MN or TN (4.2 nm), due to the larger interlayer thickness. This is due to the generation of higher concentration O radicals by N addition¹³ resulting in the formation of oxynitride interlayer, which is consistent with XPS results. Similar results were observed for fully nitrided PE-ALD TaO_xN_y .⁶

To determine the nitrogen depth profiles more precisely, angle resolved XPS was carried out by measuring the XPS peak intensity additionally at 30° detection angle. The integrated nitrogen peak intensity ratios between 30° and 90° detection angles [$I_{N(30)}/I_{N(90)}$] of BN sample is smaller than 1, indicating that the nitrided layer is located away from the surface. On the contrary, $I_{N(30)}/I_{N(90)}$ is larger than 1 for TN and MN, indicating that the nitrided layers of these samples are located closer to the surface region than BN. Especially, $I_{N(30)}/I_{N(90)}$ of TN (1.55) is larger than that of MN (1.21), indicating that the nitrided layer of sample TN is located closer to the surface than MN. These angle resolved XPS results together with the deconvoluted XPS spectra strongly suggest that the depth profile controlled nitrogen incorporation was achieved as we intended.

Figure 2(a) shows the C-V measurement results of MOS capacitors with these three films as insulators. That of PE-ALD HfO_2 is also shown as a reference. Compared to HfO_2 , the EOTs of all three samples have been reduced (1.10 nm for BN, 1.07 nm for TN, and 1.00 nm for MN). The smaller EOT of BN than that of HfO_2 is attributed to the larger dielectric constant of the interface layer. On the contrary, the smaller EOTs of TN and MN than that of HfO_2 are due to the increase in dielectric constants of the films. In addition, the larger EOT of TN than that of MN seems to be related to the postdeposition annealing process performed in this experi-

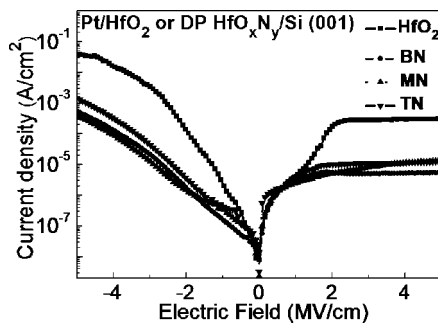


FIG. 3. Leakage current density–voltage curves of MOS capacitors with HfO_2 and DP (depth profiled controlled) HfO_xN_y as a gate insulator.

ment. Without PDA, the EOTs of TN and MN were almost the same as 1.00 nm. After PDA, however, the EOT of TN increased to 1.07 nm, while that of MN remained constant. We speculate that the increase in EOT for TN is due to the partial removal of nitrogen from the topmost nitrided layer. This agrees with a previous report on annealing of nitrided film showing significant nitrogen removal near the top surface than bulk.¹⁴ However, for MN, having a nitrided layer in the middle of the film, the nitrogen atoms are not removed by PDA.

Figure 2(a) also shows that the C - V curve of BN has the largest hysteresis of 0.12 V with $V_{\text{FB}} = -0.14$ V. This is a similar result to fully nitrided HfO_xN_y mentioned above. The large hysteresis and flatband voltage shift are due to the incorporation of too much nitrogen into the interface layer region, as mentioned above. In contrast, the V_{FB} is not shifted and the hysteresis is relatively smaller (<0.08 V) for MN and TN samples. For these samples, since nitrogen is incorporated only in the middle or top position, the interfaces are not degraded.

To compare the quality of the interfaces quantitatively, the interface state densities (D_{it}) were obtained for these samples as a function of $E_{\text{trap}} - E_i$, where E_{trap} and E_i are the trap level in the band gap and the intrinsic Fermi level of Si, respectively [Fig. 2(b)]. The D_{it} of BN is the largest in the whole half range of band gap, almost twice or more than that of TN. This result agrees with previous reports showing that the interface quality for postdeposition nitridation is better than predeposition nitridation.³ However, the best interface quality was obtained for MN (near of midgap $D_{\text{it}} = 0.7 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$) among the three. Based on XPS results, while the interface of TN is totally lack of nitrogen, MN has small nitrogen atoms incorporated into the interface region. The incorporation of proper amount of nitrogen leads to reduction of the interface states by relaxing the interfacial strain or passivating defects.¹⁵ Thus, while the D_{it} of HfO_2 and TN are almost the same with each other ($1.2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$) at the near of midgap, the MN has lower D_{it} value. The changes in D_{it} at the whole half of the band gap show the same trend with midgap D_{it} value, $\text{BN} > \text{TN} > \text{HfO}_2 > \text{MN}$.

All three samples have shown almost an order of magnitude lower leakage currents and higher dielectric breakdown voltages than PE-ALD HfO_2 . Figure 3 shows the current density–voltage measurement results for the same samples. The leakage current densities of gate injection at -1 MV/cm of all three samples were almost an order of magnitude lower than that of PE-ALD HfO_2 . Among the three samples, the leakage current density of BN sample at

-1 MV/cm was measured to be the lowest ($1 \times 10^{-7} \text{ A/cm}^2$), which is almost same as fully nitrided HfO_xN_y film, probably due to the thick interfacial layer. Meanwhile, the leakage current densities of TN ($3.5 \times 10^{-7} \text{ A/cm}^2$) and MN ($2 \times 10^{-7} \text{ A/cm}^2$) are slightly higher, but comparable to that of BN. These leakage current values are comparable to previously reported one on nitrided HfO_2 prepared by other methods such as high temperature NH_3 annealing.³

A more prominent benefit of nitrogen depth profile control is observed in the reliability. The 50% failure electric field of MN sample is improved significantly (2 MV higher) and the standard deviation of failure voltages is about 2.5 times smaller than that of HfO_2 (data not shown). Thus, the nitrogen depth profile control provides much more opportunity to tune the electrical properties of high k gate oxide. By nitrogen depth profiling, the fabrication of high k gate oxide with good properties in terms of EOT, D_{it} , and high dielectric strength is achievable, which has not been possible by other nitridation methods. The current results manifest the benefits of ALD, enabling the control of the compositional depth profiling with atomic accuracy. A similar technique would be applicable to produce nanothin films for various applications. Especially, the excellent conformality of ALD together with controllability of depth profiling is expected to greatly contribute to the fabrication of next generation devices.

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