Transactions of the Materials Research Society of Japan 30[1] 209-212 (2005)

ECR Ar/O_2 Plasma Oxidation of HfN Thin Films for High Dielectric HfO_xN_y Formations

T. Kurose, T. Uchikawa, S. Ohmi, and T. Sakai
Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology
G2-6, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8502
Phone&Fax: +81-45-924-5473, e-mail: kurose@lsi.ip.titech.ac.jp

Electron cyclotron resonance (ECR) plasma oxidation of HfN thin films was investigated for high dielectric HfO_xN_y thin films formations. After high vacuum annealing (HVA) at 700°C for 3 min followed by 1000°C post-deposition annealing (PDA) for 1 min in flowing N_2 ambient, equivalent oxide thickness (EOT) of 1.3 nm with the leakage current of 4.3 x 10^{-3} A/cm^2 (@V_{FB}-1V) was obtained, however, the V_{FB} shift still remained. It was found that the electrical characteristics were dramatically improved after 700°C HVA for 5 min followed by 1000°C PDA for 2 min for EOT of 1.4 nm with a leakage current of 2.3 x 10^{-3} A/cm^2 (@V_{FB}-1V) and a V_{FB} shift of -0.05 V.
Key words: HfON, ECR, high-k, gate dielectric, plasma oxidation

1. INTRODUCTION

SiO_2 gate dielectric has become thiner than 2 nm or less with scaling of MOSFET. It causes the increase of gate leakage current by direct tunneling conduction. Therefore, high-k gate dielectrics, such as ZrO_2, HfO_2, and La_2O_3, are being investigated as alternative gate insulators [1]. Among these materials, HfO_2 is one of the more promising materials due to its high dielectric constant (k=25) and suitable barrier heights for electrons and holes in terms of the gate insulator applications. However, HfO_2 has some problems such as crystallization by high temperature annealing, formation of an interfacial layer with a low dielectric constant, flat-band voltage (V_{FB}) shift, and boron penetration from p^+-poly Si gate. On the other hand, HfO_xN_y thin films show some advantages such as good thermal stability, suppression of the interfacial layer formation, and resistance to boron penetration [2, 3].

In this paper, HfO_xN_y high-k thin films formed by the electron cyclotron resonance (ECR) plasma oxidation of HfN thin films deposited on p/p^+-Si(100) by the ECR sputtering method are investigated. This method would be expected to form high-quality gate insulator thin films because the ECR sputtering causes little damage to the deposited films, and HfN thin films would be expected to suppress interfacial layer formation during Ar/O_2 plasma oxidation and post-deposition annealing (PDA) processes [4, 5].

2. EXPERIMENTAL PROCEDURE

The p/p^+-Si(100) wafers were chemically cleaned in H_2SO_4/H_2O_2 and dipped in diluted HF followed by a rinse in ultra-pure water (Organo UPW system). HfN thin films (1 nm) were deposited on p/p^+-Si(100) at room temperature by ECR plasma sputtering. The pressure in the chamber during the deposition was 9 x 10^{-2} Pa with Ar/N_2 flow rates of 20/8 sccm. The HfN thin films were then oxidized by ECR Ar/O_2 plasma for 60 s to form the HfO_xN_y thin films with Ar/O_2 flow rates of 20/8 sccm. The deposited HfO_xN_y films were annealed in a vacuum (10^{-4} Pa) at 700°C for 3 or 5 min (HVA). The post-deposition annealing (PDA) was also carried out by the rapid thermal annealing system (ULVAC VHC-P610) at 400 to 1000°C for 1 to 10 min in the flowing N_2 ambient. Finally, Al electrode was deposited by evaporation. The fabricated Al/HfO_xN_y/p-Si(100) MOS diodes were characterized by capacitance-voltage (C-V) and current density-voltage (J-V) measurements. C-V was measured in the frequency range of 10 k – 1 MHz by LCR meter (HP 4284A), and J-V was measured by semiconductor parameter analyzer (HP 4156A). The equivalent oxide thickness (EOT) was calculated from the obtained C-V results by using exponential potential based quantum mechanical extraction method (EPOQUE) [6]. The surface morphology of the HfO_xN_y films was observed by tapping mode AFM (Atomic Force Microscopy, Digital Instrument : Nanoscope III). XPS (X-ray Photoelectron Spectroscopy) measurement was also performed by using Al Kα non-monochromatic X-ray source.

3. RESULTS AND DISCUSSION

3.1 Effect of Post-Deposition Anneal

Figure 1 shows the AFM images for HfO_xN_y films formed by ECR plasma oxidation of the HfN thin films followed by the HVA for 3 min. The surface morphologies were found to be very smooth for the films both before and after the 1000°C PDA. The obtained rms surface roughness was approximately 0.14 nm.

Figure 2 shows PDA temperature dependence of C-V (1 MHz) and J-V characteristics for the HfO_xN_y thin films. As shown in Fig. 2(a), the V_{FB} shift was quite large in case of without PDA, while it was improved with the increase of PDA temperature. After the 1000°C PDA, the V_{FB} shift was improved to -0.44 V. Interestingly, the equivalent oxide thicknesses (EOTs) became thin with the increase of PDA temperature, and an EOT of 1.3 nm was obtained and the hysteresis width

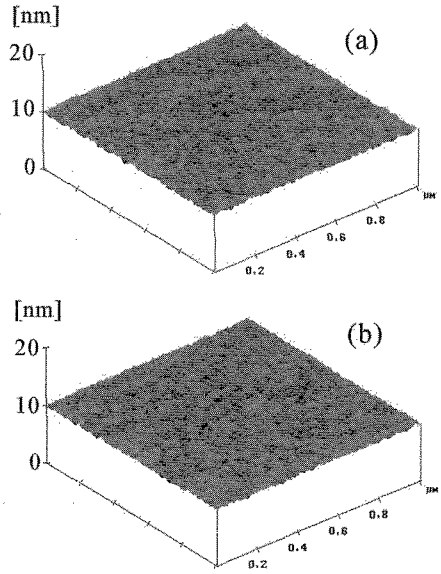

Fig. 1 AFM images for HfO_xN_y thin films(x, y: 1μm x 1μm, z: 10 nm/div.).(a) After HVA for 3 min(w/o PDA) (rms: 0.14 nm),and(b) after 1000°C PDA (rms: 0.14nm).

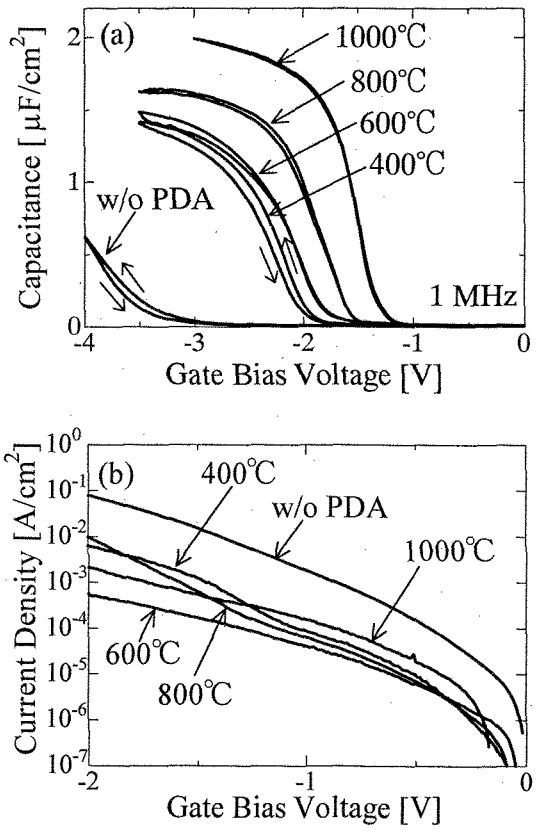

Fig. 2. PDA temperature dependence of (a) C-V (1 MHz) and (b) J-V characteristics for the HfO_xN_y thin films.

was also improved from 80 mV down to 3 mV after the 1000°C PDA. Furthermore, the leakage current density was decreased after the PDA. By performing 1000°C PDA, the leakage current was decreased to 4.3 x 10^{-3} A/cm^2 (@ V_{FB}-1V).

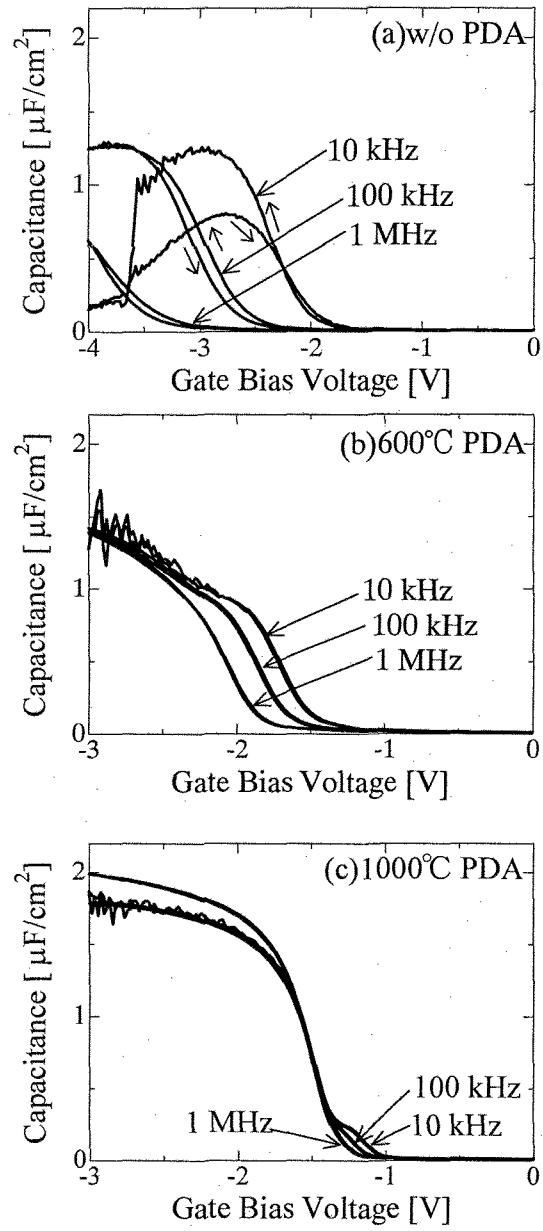

Fig. 3. Frequency dependence of C-V characteristics for the HfO_xN_y thin films, (a) without PDA, (b) 600°C PDA, (c) 1000°C PDA.

The frequency dependence of C-V characteristic for the HfO_xN_y thin films is shown in Fig. 3. The severe frequency dispersion observed in the C-V for the film without PDA (Fig. 3(a)) was significantly improved by performing the PDA. After 600°C PDA, the V_{FB} shifts with measurement frequency were clearly observed, although the hysteresis was negligible as shown in Fig. 3(b), while those were dramatically improved by the 1000°C PDA except the slight dispersion at the weak inversion region. The V_{FB} shift of -0.44 V was obtained as shown in Fig. 3(c).

Figure 4 shows the angle-resolved Si2p and Hf4f photoelectron spectra for the HfO_xN_y film without PDA. The take-off angles of XPS measurements were 30 to 80°. From the Si2p spectra, it was found that the Si-O

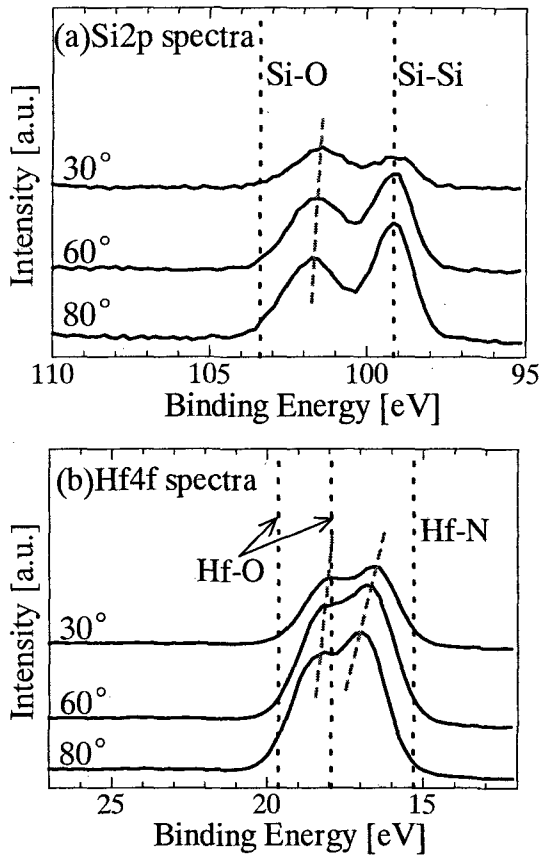

Fig. 4. Angle-resolved (a) Si2p and (b) Hf4f photoelectron spectra for HfO_xN_y films without PDA.

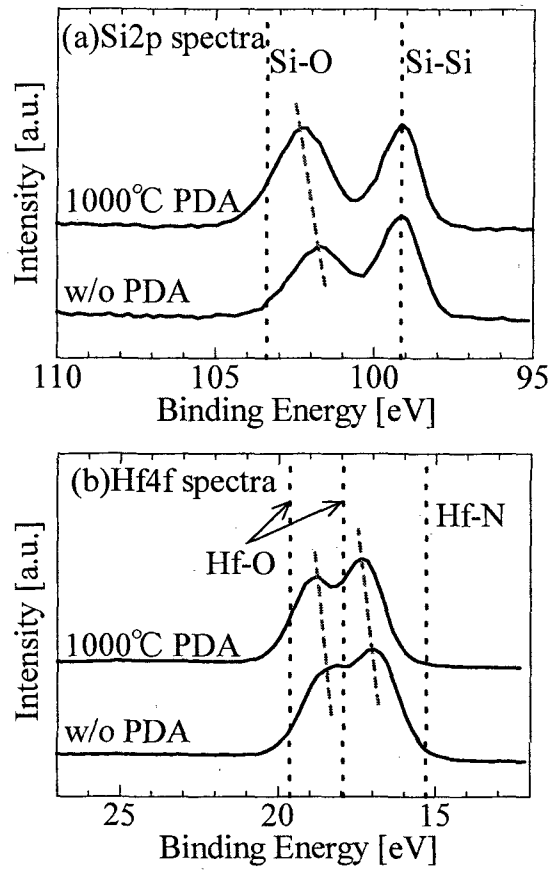

Fig. 5. Photoelectron spectra for HfO_xN_y /Si before and after the 1000°C PDA (take-off angle: 80°). (a) Si2p and (b) Hf4f.

peaks increased with the take-off angles as shown in Fig. 4(a). This result suggests the oxygen atoms diffused well into HfO_xN_y films during the Ar/O_2 plasma oxidation and HVA processes. Furthermore, from the Hf4f spectra shown in Fig. 4(b), it was confirmed that the HfN thin films were completely oxidized by ECR Ar/O_2 plasma irradiation. In addition, the nitrogen atoms were found to diffuse toward the surface and the oxygen atoms toward the interface in HfO_xN_y films by performing ECR plasma oxidation and HVA. This result suggested that Hf-O binding is dominant at the interface region, while Hf-N binding increased at the surface region.

Figure 5 shows Si2p and Hf4f photoelectron spectra (take-off angle: 80°) for the HfO_xN_y/Si after the PDA. In this measurement condition, the binding configuration close to the interface of the HfO_xN_y/Si could be observed. As shown in Fig. 5(a), the Si2p spectra peak was chemically shifted to the Si-O binding energy and its intensity became strong after performing PDA with increasing PDA temperature. The Hf4f spectra peak was also shifted to the Hf-O binding energy, as shown in Fig. 5(b). These spectra shown in Fig. 5 led to the conclusion that the oxygen diffused toward the HfO_xN_y/Si interface during the PDA so that the HfSiON interface layer was formed after the PDA.

3.2 Time Dependence of Post-Deposition Anneal

As described in the previous section, HfO_xN_y films formed by ECR Ar/O_2 plasma oxidation of the HfN thin films showed excellent electrical characteristics such as small EOT with low leakage current and small hysteresis width. However, the negative V_{FB} shift still remained. In order to suppress the V_{FB} shift, the annealing time of HVA and PDA was investigated. First of all, the HVA was carried out for 5 min for improving the characteristics of deposited films, and the 1000°C PDA, which was the temperature showed the best electrical characteristics thus far, was further investigated to have the optimum condition with increasing PDA duration in the range of 1 to 10 min.

Figure 6 shows the PDA time dependence of the C-V (1 MHz) and J-V characteristics for HfO_xN_y thin films after the HVA for 5 min. As shown in Fig. 6(a), the V_{FB} shifts in C-V characteristics were almost suppressed for each PDA duration. It was considered that the HVA for 5 min led to a reduction of the positive fixed charge that existed in the HfO_xN_y thin films. It should be noted that the C-V characteristics and the V_{FB} shift for the film without PDAs was significantly improved compared to the film after the HVA for 3 min, as shown in Fig. 2(a) and Fig. 6(a), respectively. After 1000°C PDA for 3 min, the EOT of 1.3 nm with the leakage current of 7.5×10^{-3} A/cm^2 (@ V_{FB}-1V) was obtained for the HfO_xN_y film and the V_{FB} shift was approximately -0.02 V. The C-V characteristic of the HfO_xN_y film after the 1000°C PDA for 2 min was also excellent ; the EOT of 1.4 nm with the leakage current density of 2.3×10^{-3} A/cm^2 (@ V_{FB}-1V), and the V_{FB} shift was to -0.05 V. On the other hand, after PDA for 5 min or longer, the EOTs were

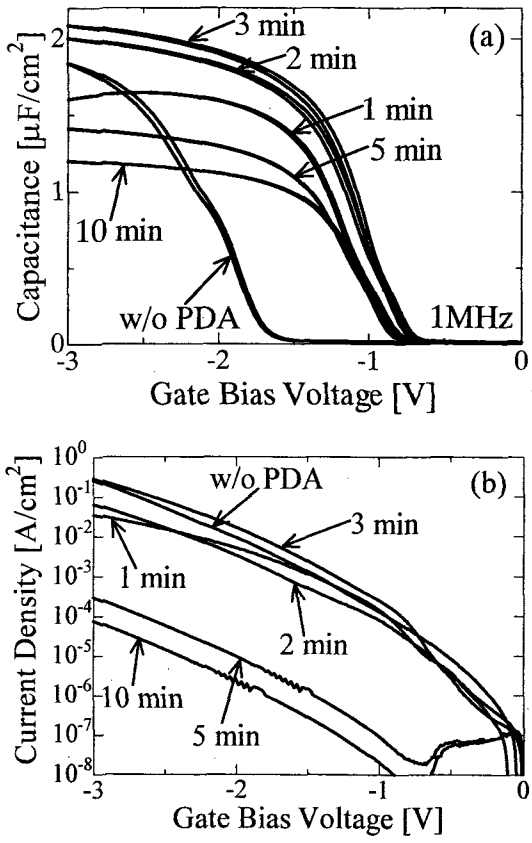

Fig. 6. Time dependence of 1000°C PDA for (a) C-V (1 MHz) and (b) J-V characteristics for HfO_xN_y thin films.

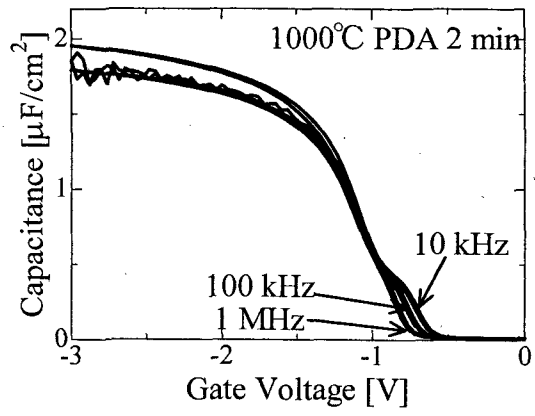

Fig. 7. Frequency dependence of C-V for the film after the 1000°C PDA for 2 min.

significantly increased to 2.1 nm or thicker, probably caused by the formation of low dielectric constant layer such as SiO_x. The remarkable reduction of the leakage current, after 1000°C PDA for 5 min or longer, also suggested the thicker interfacial layer formations. From these results, the optimum PDA condition was considered to be 1000°C for 2 min.

Figure 7 shows the frequency dependence of C-V for the film after 1000°C PDA for 2 min. Slight frequency dispersion was still observed, although the other parameters such as EOT and V_{FB} were acceptable. Therefore, further investigation will be necessary from the device application point of view; for instance, chemical oxide layer formation prior to film deposition and/or the forming gas annealing after device fabrication.

4. CONCLUSIONS

The ECR plasma oxidation of the HfN thin films deposited on p/p^+-Si(100) was investigated for high dielectric HfO_xN_y gate insulator formations. The EOT of 1.3 nm with the leakage current density of 4.3 x 10^{-3} A/cm^2 (@ V_{FB}-1V) was obtained for HfO_xN_y thin film after the 700°C HVA for 3 min followed by the 1000°C PDA for 1 min. Furthermore, the longer HVA, such as for 5 min, was found to suppress the V_{FB} shift after the 1000°C PDA. The EOT of 1.4 nm with the leakage current density of 2.3 x 10^{-3} A/cm^2 (@ V_{FB}-1V) was obtained for HfO_xN_y thin film after HVA for 5 min followed by 1000°C PDA for 2 min, which was the optimized annealing condition.

ACKNOWLEDGMENTS

The authors would like to thank Drs. K. Saito, Y. Jin, and M. Shimada with NTT for their useful discussion for this research.

REFERENCES

[1] G. D. Wilk, R. M. Wallece, and J. M. Anthony, "High-k gate dielectrics: Current status and materials properties considerations," J. Appl. Phys., vol. 89, no. 10, pp. 5243-75 (2001).

[2] C. H. Choi, T. S. Jeon, R. Clark, and D. L. Kwong, "Electrical Properties and Thermal Stability of CVD HfOxNy Gate Dielectric With Poly-Si Gate Electrode," IEEE Electron Device Lett., vol. 24, no. 4, pp. 215-217 (2003).

[3] K. Sekine, S. Inuyama, M. Sato, A. Kaneko, K. Eguchi, and Y. Tsunashima, "Nitrogen Profile Control by Plasma Nitridation Technique for Poly-Si Gate HfSiON CMOSFET with Excellent Interface Property and Ultra-low Leakage Current," IEDM Tech. Dig. pp. 103-106 (2003).

[4] S. Ohmi, G. Yamanaka, and T. Sakai, "Characterization of AlON Thin Films Formed by ECR Plasma Oxidation of AlN/Si(100)," IEICE TRANS ELECTRON. vol. E87-C, no. 1, pp. 24-29 (2004).

[5] C. L. Cheng, K. S. C. Liao, P. L. Wang, and T. K. Wang, "Physical and Reliability Characteristics of Metal-Oxide-Semiconductor Devices with HfOxNy Gate Dielectrics on Different Surface-Oriented Substrates," Jpn. J. Appl. Phys., vol. 43, no. 5A, pp. 599-601 (2004).

[6] S. Saito, K. Torii, M. Hiratani, and T. Onai, "Analytical Quantum Mechanical Model for accumulation capacitance of MOS structures," IEEE Electron Device Lett., vol. 23, no. 6, pp. 348-350 (2002).

(Received December 23, 2004; Accepted February 2, 2005)