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Extended EOT Scalability of HfON/SiON Gate Stack Down to 0.57 nm with High Carrier Mobility by Post-Deposition Annealing

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1. Introduction

Further scaling of CMOS devices requires high-k gate dielectrics with deep sub-nm equivalent oxide thickness (EOT). Recently, it is reported that post-deposition annealing (PDA) treatment is effective means to realize EOT scaling in terms of improving dielectric constant of Hf-based gate stack through crystalline phase transformation [1, 2]. Drastic reduction of EOT is reported by eliminating SiO_2-based interfacial layer (IL) [3, 4], but the interface quality seems to be degraded somewhat. In this paper, we have tried to fabricate aggressively scaled Hf-oxide gate stack by utilizing PDA to enhance its dielectric constant. We have also put emphasis on producing high quality interface by using ultra-thin SiON as starting IL.

2. Experiment

The HfO_2 films were formed on a 0.6-nm-thick SiON IL by PLCVD technique [5, 6]. Tetrakis (1-methoxy-2-methyl- 2-propoxy)-hafnium ($Hf[OC\text{-}(CH_3)_2CH_2OCH_3]_4$) was used as Hf precursor. Typical thickness of HfO_2 films investigated was 2.2 nm. After forming HfO_2 films, some samples were subjected to PDA in a Rapid Thermal Process (RTP) chamber which is connected with HfO_2 deposition chamber via transfer module. Most of the samples were then nitrided by plasma nitridation (PN), followed by post-nitridation annealing (PNA) at 1050°C in N_2 ambient. For the electrical characterization, n-FET samples were fabricated by a gate-first process flow including 950°C activation annealing. TaSiN was used as a gate electrode.

3. Results and Discussion

Figure 1 shows in-plane XRD spectra for HfO_2 films with different thickness after PDA at a temperature of 950°C. The spectra for the thicker (4.8 nm) film indicates that the monoclinic phase is dominant. On the other hand, the thinner film (2.2 nm) shows small but distinct peak indicative of the tetragonal phase, whose k-value is higher than those of monoclinic crystalline and amorphous [7]. The data suggests that thickness of HfO_2 significantly affects crystalline phase and higher k-value can be obtained by PDA treatment to thinner HfO_2 films. Figure 2 shows in-plane XRD spectra for 2.2 nm thick HfON films prepared with and without PDA prior to PN and PNA. It is observed that the tetragonal phase originated from PDA treatment is sustained even after PN and PNA. However, the peaks are rather broad for the sample without PDA, indicating nearly amorphous structure. Figure 3 shows capacitance versus gate voltage (C-V) characteristics of HfON gate dielectrics prepared with and without PDA. It is clearly observed that the capacitance of the sample with PDA is enhanced due to tetragonal phase. EOT versus gate leakage (EOT-J_G) characteristics shown in Figure 4 also indicates enhanced scalability without degrading J_G.

Effect of nitridation on electrical properties is also examined. Figure 5 shows C-V characteristics of PDA treated HfO_2 with and without PN and PNA. It is observed that HfON shows thinner EOT than HfO_2. J_G-V_G characteristics shown in Figure 6 indicate reduction of J_G for HfO_2, which suggests increase of physical thickness probably due to regrowth of IL by the gate-first process. These data suggest that IL regrowth is suppressed by nitridation. Thus, we consider that nitridation is effective to EOT scaling.

To examine the effect of PDA on HfO_2 films thinner than 2 nm, we prepared HfO_2 films by repeating ultra-thin film deposition and annealing (D/A). Figure 7 shows In-plane XRD spectra for 2.2 nm HfON films prepared by repeating deposition of around 0.6 nm thick HfO_2 layer and annealing at 750 or 950°C 4 times. Peaks attributed to tetragonal phase are observed for both conditions. However, remarkable difference is observed in C-V and EOT-J_G characteristics shown in Figures 8 and 9. EOT scalability down to 0.57 nm is observed for 950°C D/A processed sample, which is thinner than that by 750°C. The data for 750°C D/A are almost identical to those for PDA treated samples shown in Figures 3 and 4, which reflects enhancement of k-value of HfO_2 due to tetragonal phase. Further reduction of EOT by 950°C D/A process should be attributed to additional effect. It is noticeable that 950°C D/A processed sample shows shift of flat-band voltage (V_{FB}) toward negative direction as compared to 750°C D/A processed sample and that without PDA. This is likely due to reaction of ultra-thin HfO_2 film with IL [8]. We suppose that this resulted in increase of k-value of IL, which may be responsible for the extra EOT reduction observed for 950°C D/A processed sample. Consequently, it is inferred that high temperature (950°C) PDA to ultra-thin (0.6nm) HfO_2 improves k-value of both HfO_2 film and IL. I_{DS}-V_G characteristics of n-FETs with 950°C D/A processed HfON gate dielectric are shown in Figure 10. Negligible degradation in sub-threshold characteristics is caused by inferred reaction of HfO_2 and IL. Lowering of threshold voltage corresponding to V_{FB} shift is another benefit for n-FET application. Figure 11 shows effective electron mobility characteristics for n-FETs with D/A processed HfON gate dielectrics. The data for 950°C D/A processed sample shows a small degradation of electron mobility, but still the value is high as 154 $cm^2/V/s$ at E_{EFF}=0.8MV/cm. These data suggest that quality of SiON/Si interface is not severely degraded by D/A process in the present conditions.

Characteristics of HfON films prepared by D/A process with and without forming initial SiON IL are also compared in Figure 9 and 11. IL-less HfON shows a little bit lower J_G than that with SiON IL. However, it shows severe degradation in electron mobility. Therefore, HfON formation starting with SiON IL seems to be a practical solution. Electron mobility obtained in the present study is compared with previous reports [4, 9-11] in Figure 12. The present value is above the trend curve of those previously reported, which suggests formation of high quality interface by the present process using SiON layer as starting IL.

4. Conclusion

We have examined effect of PDA on ultra-thin HfO_2 films to fabricate high-k gate stack with deep sub-nm EOT. Crystallization to tetragonal phase is confirmed by PDA treatment to HfO_2 thinner than 2.2 nm which led to improvement of k-value of HfO_2. It is inferred that high-temperature (950°C) PDA applied to ultra-thin (0.6nm) HfO_2 film brings about improved k-value of IL due to reaction with HfO_2. Scalability was also improved by

nitridation. Thin HfON/SiON gate stack with EOT=0.57 nm is successfully formed by repeating ultra-thin HfO_2 deposition and high-temperature PDA. The electron mobility of this gate stack is higher than those in the previous reports. EOT reduction by improving k-value of initially formed SiO_2-based IL demonstrated in the present study is a promising solution to realize aggressively scaled high-k gate dielectric with high quality interface.

References

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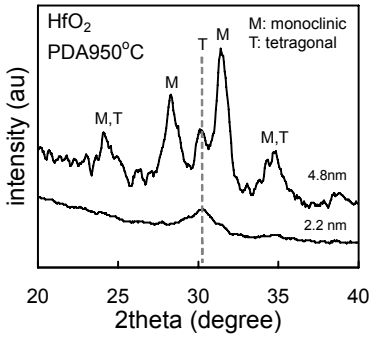

Fig. 1 In-plane XRD spectra of 4.8 nm and 2.2 nm thick HfO_2 subjected to PDA at 950°C.

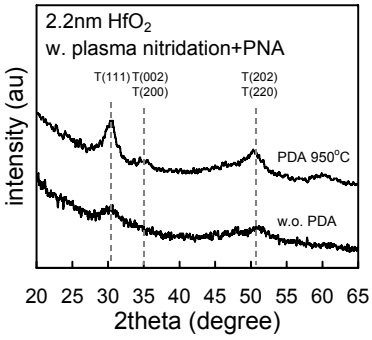

Fig. 2 In-plane XRD spectra of 2.2 nm thick HfON with and without PDA.

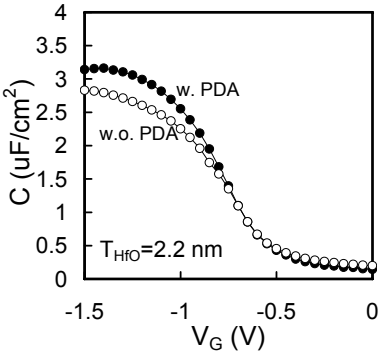

Fig. 3 C-V characteristic of 2.2 nm thick HfON with and without PDA.

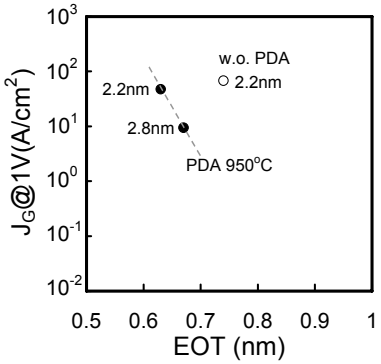

Fig. 4 EOT-J_G characteristics of the HfON films treated by PDA.

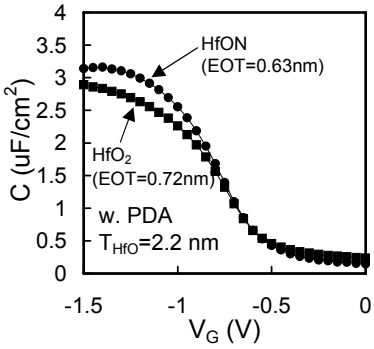

Fig. 5 C-V characteristics of PDA treated 2.2 nm thick HfON and HfO_2 films.

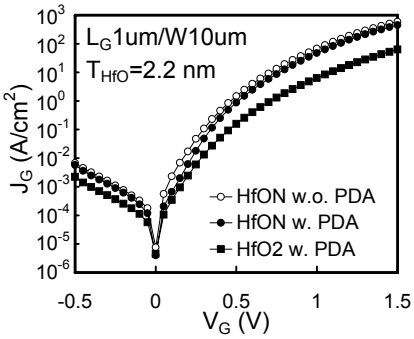

Fig. 6 I_G-V_G characteristics of HfON and HfO_2 films in the inversion region.

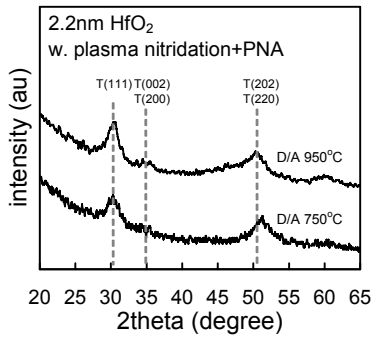

Fig. 7 In-plane XRD spectra of 2.2 nm thick HfON prepared by D/A process at 750 and 950°C.

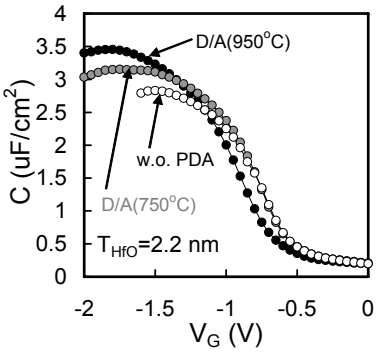

Fig. 8 C-V characteristic of 2.2 nm thick HfON prepared by D/A process.

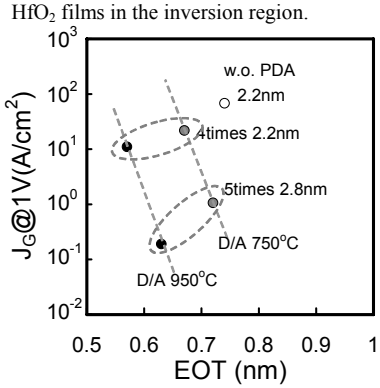

Fig. 9 EOT-J_G characteristics of the HfON films prepared by D/A process at 750°C and 950°C. The data for HfON formed without IL is shown for comparison.

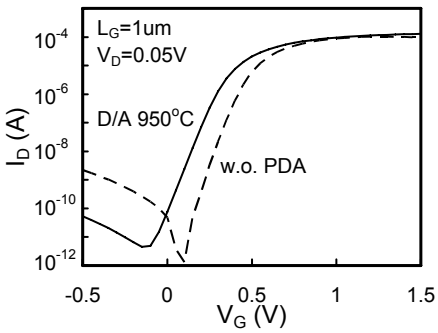

Fig. 10 I_{DS}-V_G characteristics of HfON films prepared by D/A at 950°C.

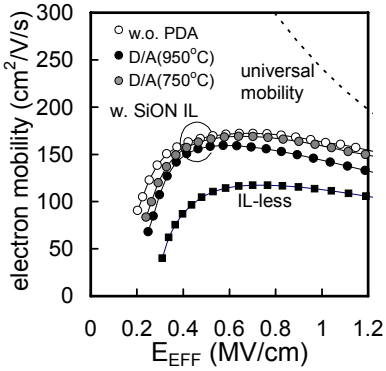

Fig. 11 Electron mobility characteristics for n-FETs with D/A processed HfON gate dielectrics. The data for HfON formed without IL is shown for comparison.

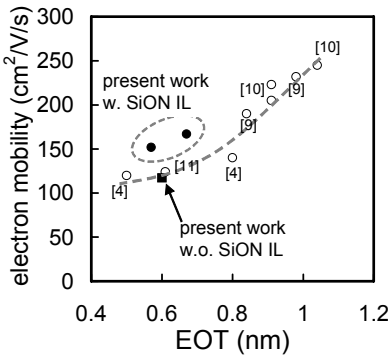

Fig. 12. Summary of electron mobility at E_{EFF}=0.8MV/cm as a function of EOT. Previous data are plotted by open circles.