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Control of Ion Bombardment and Species for Ultra Low Temperature Formation of Silicon Nitride Gate Dielectric Films Using Plasma Chemical Vapor Deposition

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1.Introduction

As device dimensions shrink below 0.1 μm in ultra large scale integrated circuits (ULSIs), the thickness of the gate dielectric film (SiO_2) in field effect transistors (FETs) will fall to be 2-3nm range, which leads to the leakage due to a tunneling current. In principle, the SiO_2 film is replaced by a dielectric film with a higher dielectric constant, since the physical thickness can be increased to be above 3nm thickness according to the scaling limit [1]. The silicon nitride (SiN_x) film attracts much attention as scaled gate dielectric films in next generation's ULSIs.

In this study, we have clarified the effects of ion bombardment and species on the film property of ultra thin SiN_x films (5nm) formed at a low temperature of 300 degree C with and without charged species in ECR-PECVD. The effect of ion bombardment and species on the growth in the ECR plasma employing N_2/SiH_4 gases was found to be much different from in that employing NH_3/SiH_4 gases. These film properties and the surface reactions for SiN_x film formation are discussed on the basis of results of the *in-situ* XPS and *in-situ* FT-IR RAS.

2.Experimental

Figure 1 shows a schematic of the experimental apparatus of typical ECR PECVD system with a divergence magnetic field used in this study. SiN_x films were formed on p-type (100) silicon substrates. Silicon substrates for *in-situ* XPS were cleaned by HF ($HF:H_2O$=1:10) solution at room temperature before deposition. To eliminate the charged species incident on the substrates in the plasma, a device, where two permanent magnets set parallel with 3cm separation, was installed at the position of 7cm above the substrate.

In this system, the process chamber was equipped with *in-situ* FT-IR RAS. The IR beam was introduced through a polarizer and a KBr window into the process chamber at an incident angle of 80°.

Furthermore, the XPS system was connected to the ECR chamber through a transfer chamber in a vacuum. Therefore, *in-situ* FT-IR RAS and XPS analyses enabled us to investigate the chemical structure of SiN_x films immediately after deposition.

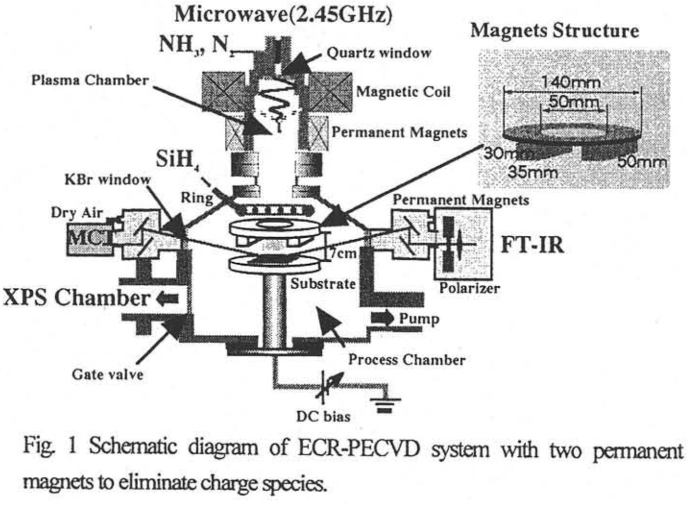

Fig. 1 Schematic diagram of ECR-PECVD system with two permanent magnets to eliminate charge species.

3.Results and Discussion

The plasma in this study was evaluated to electron temperatures below 4eV and plasma densities above 10^9 cm^{-3}.

Figure 2 shows N/Si ratios derived from *in-situ* XPS of (a) N_2/SiH_4 PECVD films formed with charged species, (b) without charged species, (c) NH_3/SiH_4 PECVD films formed with charged species, and (d) without charged species. In the case of without charged species, N/Si ratio of SiN_x films were constant, and the composition was confirmed near stoichiometry from the ratio of the N 1*s* peak to the chemically shifted Si 2*p* peak. On the other hand, N/Si ratios of SiN_x films, formed with charged species, increased with gas flow ratios (R=N_2/SiH_4, NH_3/SiH_4) between 2.5 and 10. The SiN_x films formed in the regime $20 \leqq R \leqq 33$ were near stoichiometry. The CVD conditions optimized for obtaining near stoichiometry were as follows; a total pressure : 0.5 Pa, gas flow ratio : 20, a microwave power : 300W, a substrate bias : floating, a substrate temperature : 300 degree C.

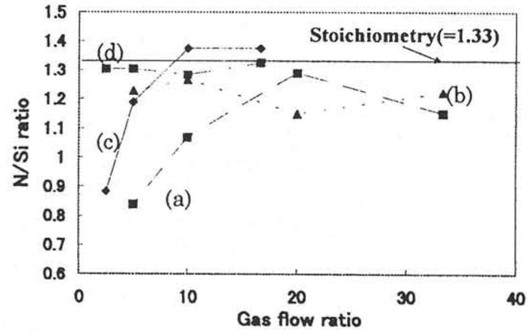

Fig. 2 N/Si ratio derived from *in-situ* XPS of (a) N_2/SiH_4 PECVD SiN_x films formed with charged species, (b) without charged species, (c) NH_3/SiH_4 PECVD SiN_x films formed with charged species, (d) without charged species.

Figure 3 shows *in-situ* FT-IR RAS spectra of (a) N_2/SiH_4 PECVD films formed with charged species, (b) without charged species, (c) NH_3/SiH_4 PECVD films formed with charged species, and (d) without charged species. The film thickness are shown in each spectrum in Fig. 2. The SiN_x film was deposited on a Al film sputtered in vacuum on a silicon substrate. In the case of N_2/SiH_4 PECVD SiN_x films, the deposition rates with and without charged species were about 3.3 nm/min and 0.35 nm/min, respectively. Si-N_x peak intensity of SiN_x films formed without charged species was strong and sharp compared with that with charged species. The frequency component appeared at 1106 cm^{-1} is due to the vibration of Si-N bonds forming the SiN_x network. In the case of NH_3/SiH_4, the deposition rates with and without charged species were about 4.3 nm/min and 1.39 nm/min, respectively. Si-N_x peak intensity of SiN_x films formed with charged species was stronger and more sharp than that without charged species. The frequency component appeared at 1096 cm^{-1} is due to the vibration of Si-N bonds forming the SiN_x network.

Figure 4 shows Si 2*p* spectra of (a) N_2/SiH_4 PECVD films formed with charged species, (b) without charged species, (c) NH_3/SiH_4 PECVD films formed with charged species, and (d) without charged species. In order to clarify the effects of ion bombardment and species on the film property of SiN_x films formed with charged species in ECR-PECVD, the film compositions were adjusted to near stoichiometry. The *in-situ* XPS results of chemical shift are summarized in Table 1. With exposure to the N_2/SiH_4 plasma, the peak shift appeared on the higher energy region. This peak shift corresponds to Si-N_x bonds. The peak shift of SiN_x films formed without charged species was higher than that with charged species, which suggests that Si-Si bonds were reduced by eliminating charged species. On the other hand, in the case of NH_3/SiH_4 plasma, the peak shift of SiN_x films formed without charged species was lower than with charged species. This fact suggests that Si-Si bonds were reduced by NH_x^+ charged species. The control of ion bombardment and species on the growth was found to be a key factor for forming the high quality ultra thin SiN_x films.

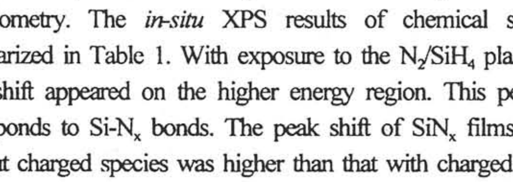

Fig. 3 Si 2*p* *in-situ* XPS spectra of (a) N_2/SiH_4 PECVD SiN_x films formed with charged species, (b) without charged species, (c) NH_3/ SiH_4PECVD SiN_x films formed with charged species, (d) without charged species.

Table 1. Chemical shift (eV) and normalized Si-N_x peak intensity

	with charged species	without charged species
N_2/SiH_4 (*in-situ* XPS)	2.7 (eV)	2.8 (eV)
(*in-situ* FT-IR RAS)	1.23	1.96
NH_3/SiH_4 (*in-situ* XPS)	3.1 (eV)	2.7eV
(*in-situ* FT-IR RAS)	2.65	1.61

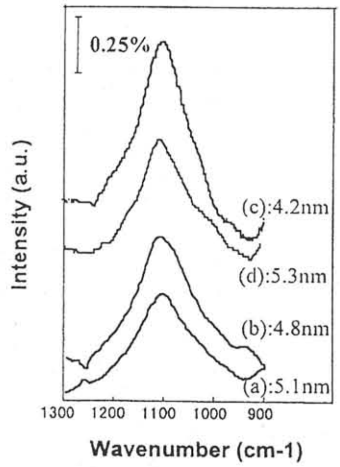

Fig. 4 *in-situ* FT-IR RAS spectra of (a) N_2/SiH_4 PECVD SiN_x films formed with charged species, (b) without charged species, (c) NH_3/SiH_4PECVD SiN_x films formed with charged species, (d) without charged species.

As for electrical property, a considerably low leakage current was observed in the case without charge species in ECR plasma employing N_2/SiH_4 gas. At a voltage of 1.5 V, the corresponding effective electric field was about 3 MV/cm for the equivalent oxide thickness (EOT) [3] of 2.5 nm. For SiN_x films formed without charged species, the current density at 3 MV/cm was 7×10^{-8} A/cm^2, which satisfied safely fulfilling requirement of less than 2×10^{-7} A/cm^2 of leakage current density at the operating electric field for 256 Mb DRAM.

4.Conclusion

We have clarified the effects of ion bombardment and species on the films property of ultra thin SiN_x films formed in ECR-PECVD at substrates at 300 degree C. As a result, the control of ion bombardment and species on the growth was found to be a key factor for forming SiN_x films at low temperatures. In the case of NH_3/SiH_4 PECVD, ions play an important role to obtain the high Si-N_x bond density. On the contrary, in the case of N_2/SiH_4 PECVD, radicals are effective to the ultra thin SiN_x film formation.

5.References

[1] D. G. Park, et al, *J. Vac. Sci. Technol.*, B14(4), pp. 2674, Jul/Aug 1996.

[2] T. P. Ma, *IEEE Trans. Electron Devices*, vol. 45, No.3, pp. 680, March 1998.