Effect of ions and radicals on formation of silicon nitride gate dielectric films using plasma chemical vapor deposition

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We have clarified effects of ions and radicals on the film property of ultrathin silicon nitride (SiN_x) films of 5 nm in thickness formed on Si substrates at 300 °C in electron cyclotron resonance plasma-enhanced chemical vapor deposition (PECVD) employing ammonia and silane (NH_3/SiH_4), and nitrogen and silane (N_2/SiH_4) gases. *In situ* Fourier transform infrared reflection absorption spectroscopy and *in situ* x-ray photoelectron spectroscopy confirmed that in N_2/SiH_4 plasma, Si-N bonds in the film were increased by eliminating charged species, and thus, radicals promoted the formation of the SiN_x film of high Si-N bond density. On the other hand, Si-N bonds in the film were decreased by eliminating charged species, and eventually, ions played an important role in forming the film of high Si-N bond density in NH_3/SiH_4 plasma. The excellent hysteresis of 0.04 V was successfully achieved with the NH_3/SiH_4 plasma. Furthermore, the quadrupole mass spectroscopy suggests that NH_4^+ charged species make a significant contribution to the formation of ultrathin SiN_x films with high quality. These results provide insights into important species to be controlled in the PECVD for low temperature formation of the SiN_x gate dielectric films in ultralarge scale integrated circuits. © *2001 American Institute of Physics.*
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I. INTRODUCTION

As device dimensions shrink below 0.1 μm in ultralarge scale integrated circuits (ULSI), the thickness of the silicon oxide (SiO_2) gate dielectric film in field effect transistors (FETs) will fall to be 2-3 nm range, which leads to the leakage due to a tunneling current. The conventional SiO_2 film has been requested strongly to be replaced by the dielectric film of a higher dielectric constant, since the physical thicknesses above 3 nm can be obtained according to the scaling limit.[1] The silicon nitride (SiN_x) film attracts the special attention as the scaled gate dielectric film in the next generation of ULSI, because of its high dielectric constant and excellent compatibility with the conventional Si wafer process. Plasma-enhanced chemical vapor deposition (PECVD) method is one of the most promising candidates to synthesize the ultrathin film with controlling the thickness and property of film precisely at a low temperature. In PECVD, ions and radicals play important roles in forming the films. In general, it has been reported that the bombardment of high energy ions causes the damage on the film property and interface between the film and substrate.[2]

Recently, Saito et al. reported that the SiN_x film was formed at 430 °C by a direct nitridation of Si wafer using the high density ($\geqslant 10^{12}$ cm^{-3}) plasma with a low ion bombardment energy (7 eV) and it was applied to the gate dielectric film in ULSI.[3] Although much work in SiN_x film formation employing PECVD has been carried out, it has not been clarified enough, what kind of ions and/or radicals are effective on the growth of ultrathin SiN_x films of high quality.[4] Therefore, it is indispensable to clarify surface reactions due to ions and radicals and that their effects on the property of ultrathin SiN_x film for the gate dielectric film in the next generation of ULSI. To get a better understanding of the formation mechanism of ultrathin film of high quality, observation using *in situ* techniques is strongly required, because the ultrathin film surface will be influenced considerably by impurities in the atmospheric condition.

However, there has been little work on clarifying the formation mechanism of the ultrathin SiN_x films with *in situ* analytical method. In this study, we have investigated effects of ions and radicals on the property of ultrathin SiN_x films of 5 nm in thickness at a low temperature of 300 °C in electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR PECVD). Comparisons of film properties and surface reactions for ultrathin SiN_x film formations with and without ions in the plasma are presented on the basis of results of *in situ* x-ray photoelectron spectroscopy (*in situ* XPS), Fourier transform infrared reflection absorption spectroscopy (*in situ* FT IR-RAS), and quadrupole mass spectroscopy (QMS) together with *C-V* measurements. Discussions are conducted on the significant difference between experimental results with and without charged species in ECR plasmas employing nitrogen and silane (N_2/SiH_4) and ammonia and silane (NH_3/SiH_4) gases. The results show that charged species of NH_4^+ in ECR NH_3/SiH_4 plasma make a significant contribution to the formation of ultrathin SiN_x of high quality.

II. EXPERIMENT

Figure 1 shows a schematic diagram of experimental apparatus of a typical ECR PECVD system with a divergence

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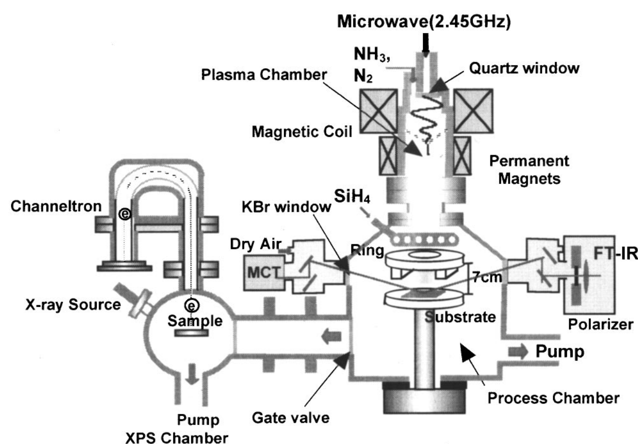

FIG. 1. Schematic diagram of ECR-PECVD system with two permanent magnets to eliminate charge species.

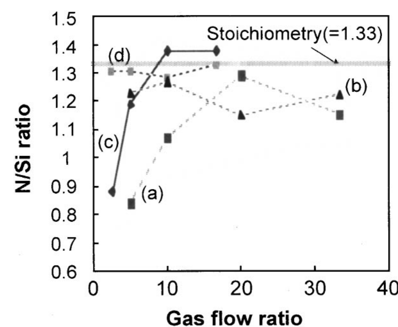

FIG. 2. N/Si ratio derived from *in situ* XPS of SiN_x films formed by (a) PECVD employing N_2/SiH_4, (b) R-CVD employing N_2/SiH_4, (c) PECVD employing NH_3/SiH_4, and (d) R-CVD employing NH_3/SiH_4.

magnetic field used in this study. The detail is described in a previous report.[5] SiN_x films were formed on *p*-type (100) silicon substrates. Silicon substrates were cleaned by HF ($HF:H_2O=1:10$) solution at room temperature before deposition. To investigate the role of ions and radicals separately in the plasma, the charged species incident on the substrates were eliminated by using a device, where two permanent magnets set parallel with 3 cm separation, were installed at the position of 7 cm above the substrate. The magnetic flux density was designed to be 0.3 T at the center of these magnets to eliminate charged species completely. Therefore, it enables us to form SiN_x films by only radicals, namely neutral radical chemical vapor deposition (R-CVD). N_2/SiH_4 and NH_3/SiH_4 were employed as feed gases. In N_2/SiH_4 gases, N_2 was introduced from the top of plasma chamber and SiH_4 was injected into the down flow plasma region, while in NH_3/SiH_4 gases, NH_3 was introduced from the top of the plasma chamber.

In this system, the process chamber was equipped with *in situ* FT IR-RAS. An IR beam was introduced into the process chamber at an incident angle of 80° through a polarizer and a KBr window. The beam was reflected at the substrate and detected by mercury–cadmium–telluride detector. The optical path was purged by the dry air to avoid the perturbation of water vapor. IR spectra were measured by FT-IR spectrometer (JIR-7000 of JEOL Co.). The wave number resolution of FT IR-RAS was 4 cm^{-1}. The double-layered substrate consists of aluminum (Al) (600 nm thickness) and *p*-type (100) silicon substrate was used. Al films were sputtered on the silicon substrate in vacuum. The dimension of substrate was 4 cm×4 cm. The FT IR-RAS has been applied for *in situ* observation of the growth process of SiN_x films in ECR PECVD conditions. The typical ECR-PECVD conditions were as follows: total pressure of 0.5 Pa, microwave power of 300 W, substrate bias of floating, substrate temperature of 300 °C and gas flow ratios of N_2/SiH_4 or NH_3/SiH_4 gases between 2.5 and 17.

Furthermore, the XPS system was connected to the ECR chamber through a transfer chamber in vacuum. In the XPS system (Escalab 220i-XL of FISONS Co.), Mg $K\alpha$ line was used as an x-ray source. The SiN_x films formed in plasma chamber were transferred to the XPS chamber without atmospheric exposure. Therefore, *in situ* FT IR-RAS and XPS analyses enable us to investigate the chemical structure of SiN_x films immediately after deposition.

Device characteristics were measured by the high-frequency *C–V* characteristics. The substrate used for *C–V* measurement was 4 cm×4 cm *p*-type (100) silicon substrate. *C–V* characteristics were obtained with a commercial measurement system (SSM 5100 system), where a mercury (Hg) electrode was placed on the sample instead of depositing a gate electrode. The area of the Hg electrode was controlled by N_2 gas pressure in the capillary. In these samples, post-metal annealing treatments were not performed.

Furthermore, ionic species were measured by quadrupole mass spectroscopy (QMS). The mass spectrometer (ANELVA AQA-360) was attached to the substrate holder with the orifice of 0.3 mm in diameter. The inside of the mass spectrometer was pumped by a 50 l/s turbo-molecular pump. The substrate holder is kept at room temperature. The ionic species effused from the plasma through the orifice were introduced into the spectrometer.

III. RESULTS AND DISCUSSION

The plasma parameters employing a pure N_2 gas in this study were evaluated to be electron temperatures (*Te*) below 4 eV, plasma density (Ne) of 3×10^9 cm^{-3} and sheath voltage of about 17 V using single Langmuir probe.

Figure 2 shows N/Si ratios derived from *in situ* XPS of SiN_x films formed by (a) PECVD employing N_2/SiH_4, (b) R-CVD employing N_2/SiH_4, (c) PECVD employing NH_3/SiH_4, and (d) R-CVD employing NH_3/SiH_4. In the case of R-CVD, that is, without charged species, the ratio (N/Si) of N 1*s* peak over the Si 2*p* one of SiN_x films was constant over the variation of gas flow rate, and the composition of film was near stoichiometry (N/Si:1.33). On the other hand, N/Si ratios of SiN_x films, formed with PECVD, increased with increasing gas flow ratio ($R=N_2/SiH_4$, NH_3/SiH_4) between 2.5 and 10. This trend is consistent with results reported earlier within slight difference in absolute values.[6,7] The SiN_x films formed in the regime of $20\leq R\leq33$ were near stoichiometry. Therefore, we have successfully controlled the thickness and composition of films in both cases with and without charged species in ECR-PECVD

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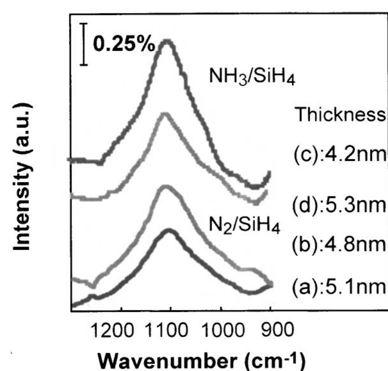

FIG. 3. *In situ* FT-IR RAS spectra of SiN_x films formed by (a) PECVD employing N_2/SiH_4, (b) R-CVD employing N_2/SiH_4, (c) PECVD employing NH_3/SiH_4, and (d) R-CVD employing NH_3/SiH_4.

employing N_2/SiH_4 and NH_3/SiH_4 gases. Here, we will focus on films of near stoichiometry, which were used throughout the present experiment. The CVD condition optimized for obtaining near stoichiometry was as follows: total pressure of 0.5 Pa, gas flow ratios of $N_2/SiH_4=100/5$ sccm ($R=20$) or $NH_3/SiH_4=50/3$ sccm ($R=17$), microwave power of 300 W, substrate bias of floating and substrate temperature of 300 °C.

Figure 3 shows *in situ* FT IR-RAS spectra of SiN_x films formed by (a) PECVD employing N_2/SiH_4, (b) R-CVD employing N_2/SiH_4, (c) PECVD employing NH_3/SiH_4, and (d) R-CVD employing NH_3/SiH_4. Film thickness is shown in each spectrum in Fig. 4. The SiN_x film was deposited on an Al film sputtered on a silicon substrate in vacuum. In the case of N_2/SiH_4 gases, the deposition rates with and without charged species were about 3.3 nm/min and 0.35 nm/min, respectively. The frequency component which appeared at 1106 cm^{-1}, is due to the vibration of Si-N bonds forming the SiN_x network. The Si-N_x peak intensity of films formed without charged species was strong and sharp compared with that with charged species. In the other case of NH_3/SiH_4 gases, the deposition rates with and without charged species were about 4.3 nm/min and 1.39 nm/min, respectively. The decrease in deposition rate of films formed without charged species in N_2/SiH_4 plasma is more remarkable than that of films formed in NH_3/SiH_4. This fact suggests that the contribution of ions to the deposition rate in the plasma employing N_2/SiH_4 is larger, than that in the plasma employing NH_3/SiH_4. The frequency component which appeared at 1096 cm^{-1} is due to the vibration of Si-N bonds forming the SiN_x network.[8] The Si-N_x peak intensity of films formed with charged species was strong and sharp compared with that without charged species. It is worth noting that the Si-N_x peak intensity in films of the same thickness (5 nm) formed with and without charged species indicated the different tendency between in N_2/SiH_4 and in NH_3/SiH_4 gases.

XPS spectra of SiN_x films formed by (a) PECVD employing N_2/SiH_4, (b) R-CVD employing N_2/SiH_4, (c) PECVD employing NH_3/SiH_4, and (d) R-CVD employing NH_3/SiH_4 are shown in Fig. 4. The Si 2*p*, Si 2*s*, N 1*s* signal and only small amount of O 1*s* peak (~1 at.%) were observed. We consider that this oxygen signal is not involved

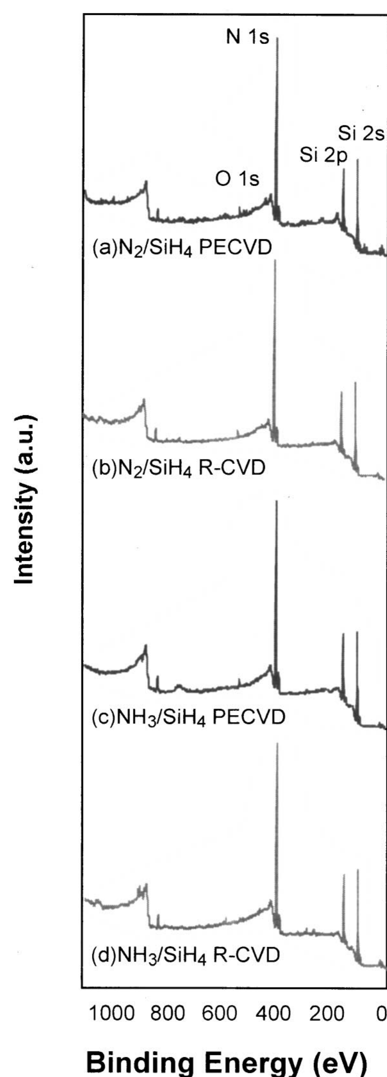

FIG. 4. XPS spectra of SiN_x films formed by (a) PECVD employing N_2/SiH_4, (b) R-CVD employing N_2/SiH_4, (c) PECVD employing NH_3/SiH_4, and (d) R-CVD employing NH_3/SiH_4.

in the deposition but comes from the oxygen absorbed on silicon surface before deposition because XPS was carried out by *in situ* observation and oxygen peaks were not observed for relatively thick films (above 20 nm). Thus, the effect of oxygen on the film properties can be neglected in this study.

Figure 5 shows Si 2*p* spectra of SiN_x films formed by (a) PECVD employing N_2/SiH_4, (b) R-CVD employing N_2/SiH_4, (c) PECVD employing NH_3/SiH_4, and (d) R-CVD employing NH_3/SiH_4. These spectra were obtained at a photoelectron takeoff angle of 90° in *in situ* XPS. In order to clarify the effects of ion bombardment and radicals on the film property of SiN_x films, film compositions were adjusted to near stoichiometry by changing the gas flow ratio. The chemical shifts in *in situ* XPS measurements are summarized in Table I. In the case of PECVD employing N_2/SiH_4, the peak shift appeared on the higher energy region. The charge transfer from Si atom to more electronegative N ones leaves a positive charge on the Si atom, which results in a shift of Si core level toward higher binding energies. Thus, it is ex-

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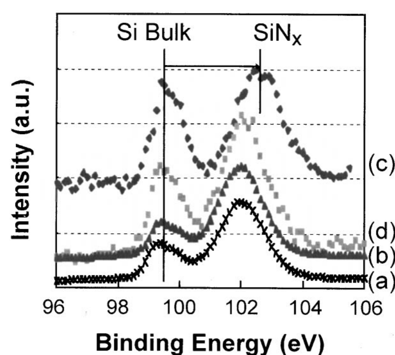


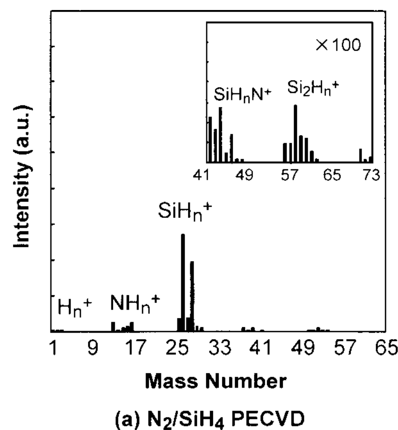
FIG. 5. Si 2*p* spectra of SiN_x films formed by (a) PECVD employing N_2/SiH_4, (b) R-CVD employing N_2/SiH_4, (c) PECVD employing NH_3/SiH_4, and (d) R-CVD employing NH_3/SiH_4.

pected that five principal components Si_0, Si_1, Si_2, Si_3, Si_4, shifted chemically, due to Si atoms which are corresponding to zero, one, two, three, or all four Si-Si bonds, respectively, have been replaced by Si-N bonds.[9] Therefore, peak shifts obtained in this study are considered to correspond to Si-N_x bonds. The peak shift of SiN_x films formed without charged species was higher than that with charged species. The fact suggests that Si-Si bonds are 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 that with charged species. Therefore, Si-Si bonds in the films are reduced by charged species such as NH_x^+ ions. It is worth noting that as the Si-N intensity is higher, the chemical shift of film is larger. It is known that the surface state trapping, which degrades the electrical property, is produced by Si-Si bonds in the silicon oxide film. Therefore, the control of ion bombardment and radicals on the film growth was found to be a key factor for forming ultrathin SiN_x films of high quality.

In order to clarify the influence of ion species on the film formation, ions incident on the substrate were measured by QMS. Figure 6 shows mass spectra for (a) PECVD employing N_2/SiH_4 and (b) NH_3/SiH_4 gases in the mass/charge (*m/z*) range between 1 and 80. The plasma condition was as follows: total pressure of 0.5 Pa, gas flow rate of N_2/SiH_4 = 100/5 sccm and NH_3/SiH_4 = 50/3 sccm, microwave power of 300 W, and substrate bias of floating. There were not any peaks above mass number of 100. SiH_n^+ ions ($n=1-3$) at 29–31 were dominantly observed. Additionally, there were peaks of SiH_nN^+ ions ($n=1-4$) at 43–46, $Si_2H_n^+$ ions ($n=1-5$) at 57–61 and $Si_2NH_n^+$ ions ($n=0-2$) at 70–72.[10] On the other hand, in the case of NH_3/SiH_4 gas, NH_4^+ ions at 18 were prominently observed. Additionally, there were weak peaks of SiH_n^+ ions ($n=1-3$) at 29–31, SiH_nN^+ ions

TABLE I. Chemical shift (eV) and normalized Si-N_x peak intensity.

	PECVD	R-CVD
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)	2.7 (eV)
(*in situ* FT IR-RAS)	2.65	1.61



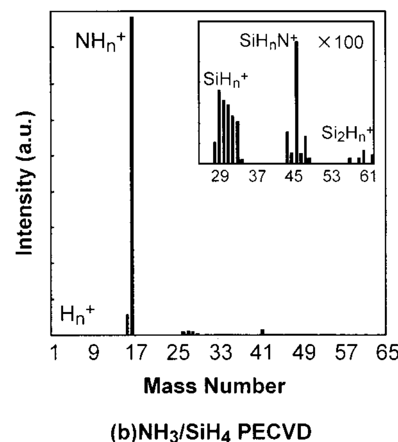


FIG. 6. Mass spectra of (a) N_2/SiH_4 (=100/5 sccm) PECVD, (b) NH_3/SiH_4 (=50/3 sccm) PECVD operating at total pressure of 0.5 Pa, microwave power of 300 W, and substrate bias of floating.

($n=1-4$) at 43–46 and $Si_2H_n^+$ ions ($n=1-5$) at 57–61. It is reasonable that we could not detect any peaks due to ions in PECVD without charged species. These results confirmed that charged species incident on the substrate were eliminated completely during the growth in R-CVDs while a lot of NH_4^+ ions were generated during the growth in PECVD employing NH_3/SiH_4. In the case of PECVD employing NH_3/SiH_4, the highest Si-N bond intensity with the largest chemical shift was observed as shown in Table I. This fact suggests that Si-Si bonds contributing to surface state trapping the SiN_x film were considerably reduced by NH_4^+ ions. It is known that NH_4^+ ion is terminal species and hence by the precursor to the deposition is believed to be the aminosilane complexes, which were formed through the reaction between NH_4^+ and SiH_n^+ ions and/or SiH_n radicals, described above. Smith et al. found that $SiH_{4-n}(NH_2)_n$ and disilane were the most plentiful products in PECVD employing NH_3/SiH_4.[10] Thus, NH_4^+ charged species play important roles in the formation of Si-N network for forming of SiN_x film of high quality, which is supported by Kushner.[11]

The high-frequency *C–V* characteristics of films were evaluated for investigating the electrical trap in films. Figure 7 shows typical *C–V* curves recorded at a high frequency of 0.1 MHz for SiN_x films formed by (a) R-CVD employing N_2/SiH_4 and (b) PECVD employing NH_3/SiH_4. The series resistance effect is corrected in these *C–V* curves. The gate

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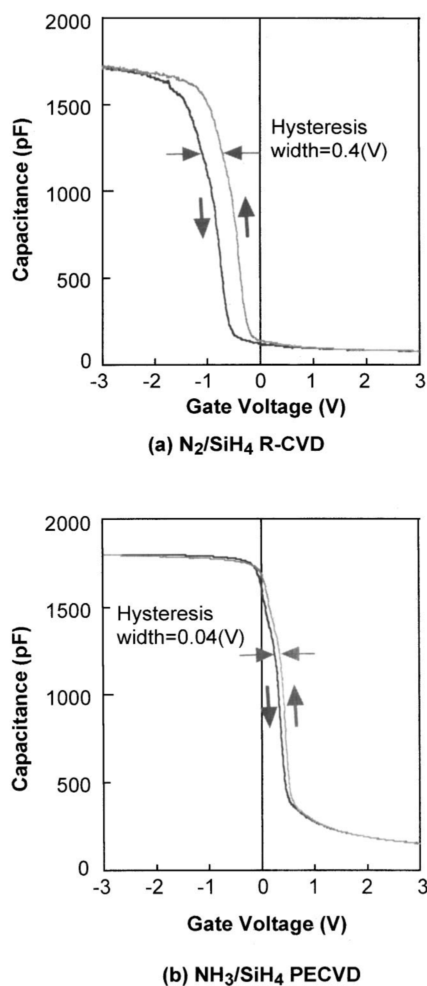

FIG. 7. Typical capacitance–voltage curves of metal–insulator–semiconductor capacitors recorded at 0.1 MHz for SiN_x films formed by (a) R-CVD employing N_2/SiH_4 and by (b) PECVD employing NH_3/SiH_4.

voltage was swept from inversion to accumulation and back at a rate of 1250 mV/s. The direction of the voltage sweep is indicated by arrows in the figures. Both samples exhibit the behavior of counterclockwise hysteresis loop direction, which is caused by surface state trapping.[12] This hysteresis value of film formed by R-CVD employing N_2/SiH_4 was 0.4 V, while the excellent hysteresis value of 0.04 V was successfully achieved for the film formed by PECVD employing NH_3/SiH_4. The areas of Hg electrode in samples of R-CVD and PECVD were about 1.75×10^{-3} and 1.65×10^{-3} cm^2, respectively. These results suggest that the state trapping density in SiN_x films formed by ECR-PECVD employing NH_3/SiH_4 is much lower than that by R-CVD employing N_2/SiH_4. The trend of hysteresis value was well corresponding to the result of Si 2*p* chemical shift measured by *in situ* XPS. Thus, the large chemical shift of Si 2*p* indicates the smaller hysteresis value. Si dangling bonds in the film are generated by a lot of Si-Si bonds and thus would act on the electrical trap. The electrical trap would be reduced by the enhancement of Si-N network and associated by hydrogen passivation effect on the Si dangling bond. As for the fixed charge density in the film, the value estimated from the flat-band voltage of high-frequency C–V was also much lower (2.44×10^{12} cm^{-2}) in the SiN_x films formed by ECR-PECVD employing NH_3/SiH_4.

Consequently, on the basis of characterization of properties of ultrathin film connecting with surface reactions, NH_4^+ charged species played important roles in the formation of Si-N network for SiN_x ultrathin film of high quality.

IV. CONCLUSIONS

We have investigated the properties and the formation mechanism of ultrathin SiN_x films of 5 nm in thickness formed on Si substrate at 300 °C in PECVD and R-CVD employing N_2/SiH_4 and NH_3/SiH_4 gases. By installing permanent devices above the substrate, charged species incident on the film surface were completely eliminated and so effects of ions and radicals on the film formation were clarified. The stoichiometric structure was successfully formed in PECVD and R-CVD changing the gas flow ratio of N_2/SiH_4 and NH_3/SiH_4. Using *in situ* FT IR-RAS and *in situ* XPS, the structures of films formed with PECVD and R-CVD were compared. Ions played an important role in obtaining the high Si-N_x bond density in PECVD employing NH_3/SiH_4, while radicals were effective in that employing N_2/SiH_4. As for the state trapping in the film, the excellent hysteresis of 0.04 V was successfully achieved with employing NH_3/SiH_4. On the basis of gas phase characterization using QMS, it was found that NH_4^+ charged species play a significant role in the forming of SiN_x film with high quality. As a result, the control of ions and radicals on the film growth was found to be a key factor for forming ultrathin SiN_x films at low temperatures for gate dielectric film in the next generation of ULSI.

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