Formation of silicon nitride gate dielectric films at 300 °C employing radical chemical vapor deposition

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(Received 10 December 1999; accepted 26 June 2000)

Silicon nitride (SiN_x) ultrathin gate dielectric films for ultralarge-scale integrated circuits have been successfully formed by radical chemical vapor deposition (R-CVD) at 300 °C. In this process, charged species incident on the silicon (Si) substrate during the growth were eliminated with the magnetic field in electron cyclotron resonance plasma-enhanced CVD employing nitrogen and silane (N_2/SiH_4) gases. By using R-CVD, SiN_x films with very low leakage current and near-ideal dielectric constant ($\epsilon=7.2$) have been obtained. *In situ* Fourier transform infrared reflection absorption spectroscopy (FT-IR RAS) has confirmed that the Si–N bonds are increased and the voids in films are reduced by eliminating charged species. A key factor for forming ultrathin SiN_x films of high quality at 300 °C is discussed, based on characterization of films synthesized with and without charged species on the substrate using *in situ* x-ray photoelectron spectroscopy, *in situ* FT-IR RAS, and *in situ* atomic force microscopy. © *2000 American Vacuum Society.* [S0734-211X(00)02105-3]

I. INTRODUCTION

As device dimensions shrink below 0.1 μm in ultralarge-scale integrated (ULSI) circuits, the thickness of the gate dielectric film (SiO_2) in field effect transistors (FETs) will fall to the 2–3 nm range. This situation, in turn, leads to leakage due to the tunneling current and penetration of boron atoms into the surface-channel *p*-type metal–oxide–semiconductor FETs with P^+ gate. A new dielectric film with higher dielectric constant is expected to be used instead of the SiO_2 film, because the thickness can be increased to above 3 nm, according to the scaling limit.[1] Silicon nitride (SiN_x) film is one of the most attractive candidates because of its high dielectric constant and its compatibility with the conventional process in ULSI. Furthermore, the SiN_x film has a high diffusion barrier for the boron penetration encountered for P^+ gate integration. Therefore, the SiN_x film attracts much attention as a scaled gate dielectric film in the next generation of ULSI. The SiN_x film deposited by low-pressure chemical vapor deposition (LPCVD) has been studied widely as a dielectric film for a dynamic random access memory (DRAM) capacitor. However, the LPCVD method requires high temperatures between 700 and 800 °C for forming SiN_x film with good quality. The high-temperature SiN_x formation process causes the change of the channel impurity profile formed in the substrate. To prevent short channel effects, all manufacturing processes, including the gate insulator formation, must be performed at a thermal budget as low as possible. Therefore, the plasma-enhanced chemical vapor deposition (PECVD) method is the most attractive candidate for the low-temperature process. However, this PECVD method has two main disadvantages: (a) produced films have high concentrations of bonded hydrogens, and (b) surface damage can be caused by the bombardment of high-energy ions, which leads to a high density of interface states.[2] Saito *et al.* reported that SiN_x films were formed at 430 °C by direct nitridation, employing high-density ($\geqslant 10^{12}$ cm^{-3}) plasma with a low ion bombardment energy (7 eV).[3] Although many studies have been done on the application of PECVD to SiN_x film formation, the effect of charge species on the growth of SiN_x in PECVD has never been investigated.

In this study, we successfully synthesized SiN_x films with low leakage current, ideal dielectric constant, and high density of Si–N bonds on silicon substrates at an ultralow temperature of 300 °C. The SiN_x ultrathin films were formed by radical chemical vapor deposition (R-CVD), where charged species incident on the substrate were eliminated during the growth in electron cyclotron resonance (ECR) nitrogen and silane (PECVD)(ECR N_2/SiH_4 PECVD). The electrical properties of films formed by R-CVD and ECR-PECVD were studied by current density-electrical field ($J-E$) and high-frequency capacitance–voltage ($C-V$) measurements. The structure of films and the surface reaction in R-CVD and ECR-PECVD are discussed, based on results from *in situ* x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and Fourier transform infrared reflection absorption spectroscopy (FT-IR RAS).

II. EXPERIMENT

Figure 1 shows a schematic diagram of the experimental apparatus of a typical ECR-PECVD system with a divergence magnetic field used in this study. Microwave power at a frequency of 2.45 GHz was introduced into the ECR chamber through a quartz window. The ECR chamber has an inner diameter of about 150 mm and a height of 160 mm. The ECR chamber was mounted on a deposition chamber. The permanent magnets surrounding the ECR chamber were used

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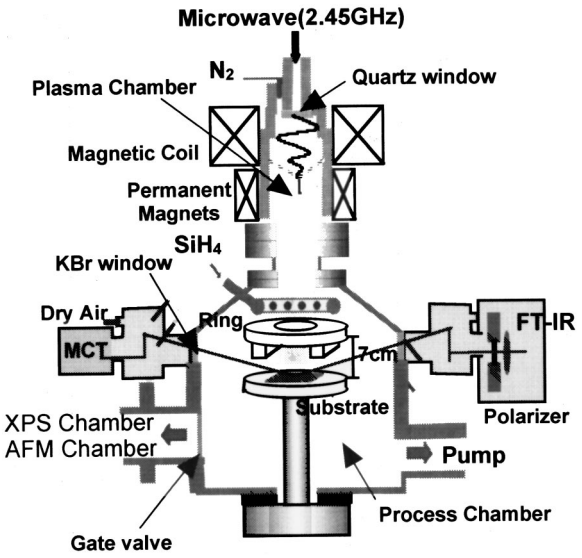


FIG. 1. Schematic diagram of ECR-PECVD system with two permanent magnets to eliminate charged species.

for the plasma confinement. The plasma stream was extracted from the ECR chamber into the deposition chamber by a divergent magnetic field. The chamber was pumped by a 1130 L/s turbomolecular pump to achieve a base pressure of 1×10^{-5} Pa. Nitrogen gas was fed into the ECR chamber through a shower nozzle near the quartz window. Silane gas was introduced into the deposition chamber near the substrate. The details were described in a previous article.[4] The plasma parameters near the substrate were measured with a Langmuir probe. A cylindrical tungsten wire 0.5 mm in diameter and 5 mm in length extending from a ceramic insulator was used as a Langmuir probe. The probe was positioned 10 mm above the substrate. The plasma was adjusted to the most suitable condition for SiN_x film formation at 300 °C. *P*-type silicon substrates used for *in situ* XPS, AFM, $J-E$, and $C-V$ measurements were cleaned by a hydrofluoric (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 consisting of two permanent magnets set parallel, with 3 cm separation, was positioned 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. In this case, SiN_x films are formed without charged species, namely, with neutral radicals (R-CVD).

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°. The beam was reflected at the substrate and detected by a mercury–cadmium–telluride detector. The optical path was purged by dry air to avoid the perturbation of water vapor. IR spectra were measured by a FT-IR spectrometer (JIR-7000, JEOL Co.). The wave number resolution used in this study was 4 cm^{-1}. For the FT-IR RAS measurement, the double-layered substrate consisted of an aluminum (Al) (600 nm thickness) film and *p*-type (100) silicon substrate. The Al films were formed by sputtering an Al target in vacuum on the silicon substrate. The dimensions of the substrate were 4 cm×4 cm. The FT-IR RAS has been applied to the *in situ* observation of the growth process of SiN_x films under ECR N_2/SiH_4 PECVD conditions.

Furthermore, an XPS system was connected to the ECR chamber through a transfer chamber in a vacuum. In the XPS system (Escalab 220i-XL of FISONS Co.), the Mg $K\alpha$ line was used as an x-ray source. The SiN_x films formed by ECR N_2/SiH_4 PECVD were transferred to the XPS chamber without any atmospheric exposure. The surface morphology and root mean square (rms) for estimating the roughness were evaluated by an AFM operated in an ultrahigh vacuum ($\leqslant 4\times10^{-7}$ Pa). The AFM apparatus was also connected to the ECR chamber, and the samples formed in the ECR chamber were transferred to the AFM chamber without exposure to the air in a vacuum and were measured by *in situ* XPS, as well. Therefore, *in situ* XPS, *in situ* AFM, and *in situ* FT-IR RAS analyses enabled us to investigate the chemical structure of SiN_x films without the influence of impurities after deposition. Metal–insulator–semiconductor (MIS) devices were obtained as follows: the substrates used were *p*-type (10 Ω cm, 100 orientation). The native oxide was stripped with a HF ($HF:H_2O=1:10$) solution for 1 min at room temperature, followed by a 3 min rinse in de-ionized water. SiN_x films 5 nm in thickness were deposited on the top of the Si surface. An ellipsometry (at $\lambda=632.8$ nm) apparatus was used to evaluate the SiN_x film thickness.

Electrical properties of films were evaluated by measuring the $J-E$ and high-frequency $C-V$ characteristics. The substrates used for $J-E$ and $C-V$ measurements were 4 cm×4 cm *p*-type (100) silicon wafers, to investigate the effect of charged species incident on the substrate during SiN_x formation. $J-E$ and $C-V$ characteristics were obtained by a commercial measurement system (SSM 5100 system). In this system, instead of depositing a gate electrode, $J-E$ and $C-V$ measurements were performed with a mercury (Hg) electrode placed above the sample. The area of the Hg electrode was controlled by N_2 gas pressure in the capillary. The frequency of the ac signal was 0.1 MHz.

Furthermore, ionic species incident on the films were measured by quadrupole mass spectroscopy (QMS). The mass spectrometer (ANELVA AQA-360) was attached to the substrate holder with a 0.3-mm-diam orifice. The inside of the mass spectrometer was pumped by a 50 L/s turbomolecular pump. The ionic species effused from the plasma to the substrate electrode through the orifice were introduced into the spectrometer and measured at room temperature.

III. RESULTS AND DISCUSSION

Plasma parameters in the ECR nitrogen (N_2) plasma were measured by the Langmuir probe. The N_2 plasma condition was as follows: total pressure of 0.5 Pa, N_2 gas flow rate of 100 sccm, microwave power of 300 W, substrate bias of floating, and substrate temperature of 300 °C, which was the optimum condition employing N_2/SiH_4 in this study. This

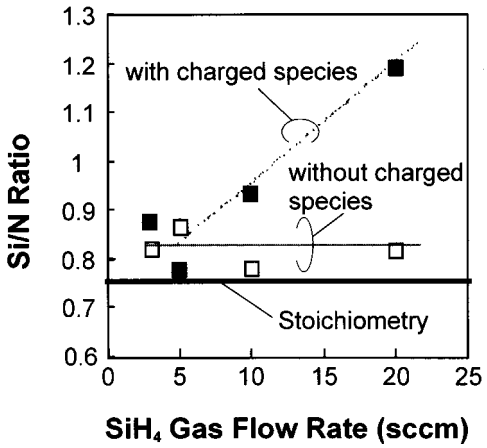


FIG. 2. N/Si ratio derived from *in situ* XPS of ECR-PECVD SiN_x films formed: (a) with charged species; (b) without charged species.

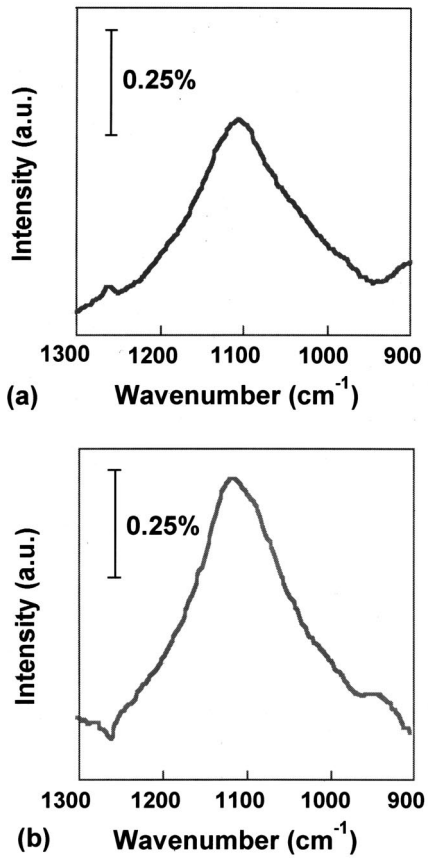


FIG. 3. *In situ* FT-IR RAS spectra of ECR-PECVD SiN_x films formed: (a) with charged species; (b) without charged species.

plasma was characterized by electron temperatures (Te) below 4 eV, a sheath voltage of about 17 V, and plasma densities (Ne) of about 3×10^9 cm^{-3}.

Figure 2 shows Si/N ratios of SiN_x films as a function of SiH_4 gas flow rate, with a N_2 flow rate fixed at 100 sccm. In the case without charged species, the Si/N ratio in SiN_x films is constant over the variation of SiH_4 gas flow rates from 3 to 20 sccm, and it is evaluated to be near stoichiometry (0.75) from the ratio of the N 1*s* peak to the chemically shifted Si 2*p* peak. The Si 2*p* spectrum of the substrate showed a peak at 99.4 eV. With exposure to the N_2/SiH_4 plasma, the peak shifted to the higher energy region. The peak shift corresponded to Si–N_x bonds. These spectra were evaluated at a photoelectron take-off angle of 90°. On the other hand, Si/N ratios in SiN_x films formed with charged species increased with SiH_4 gas flow rates between 3 and 20 sccm. The SiN_x films formed in the regime from gas ratio of 20 (100/5 sccm) to 33 (100/3 sccm) indicated near stoichiometry. This trend is similar to the result of Garcia *et al.*[5] except for a slight difference of the absolute values. It is well known that the film composition is one of the most important factors influencing the leakage current between the SiN_x film and Si substrate.[6] In this study, therefore, to clarify the effect of ion bombardment on the electrical property of SiN_x films formed with charged species in ECR-PECVD, the film compositions were adjusted to near stoichiometry.

Figure 3 shows *in situ* FT-IR RAS spectra of SiN_x films formed (a) with charged species and (b) without charged species. The deposition rates with and without charged species were about 3.3 and 0.35 nm/min, respectively. The deposition rate of the SiN_x films formed without charged species decreased to 1/10 that of films formed with charged species. The increase of deposition rate with charge species was caused by the enhanced deposition of neutral radicals, because the direct deposition of ions was small due to the lower ion densities in this study. The SiN_x film 5 nm in thickness was deposited on an Al film sputtered on a silicon substrate in vacuum. In both cases, with and without charged species, the strong absorption bands ascribed to the Si–N stretching mode are observed. The frequency component that appeared at 1130 cm^{-1} is considered to be due to the vibration of Si–N bonds in the SiN_x network. The Si–N bond peak intensity of SiN_x films formed without charged species is higher than that with charged species. The Si–N bond peak of SiN_x films formed without charged species is sharper than that with charged species. As for hydrogen bonds, it was reported that hydrogen bonds in SiN_x films deposited by CVD appeared at vibrational bands of Si–H (2160 cm^{-1}) and N–H (3355 cm^{-1}) bonds.[7] It is noteworthy that no bonds of hydrogen (Si–H_x and N–H_x) were found in the SiN_x films. Furthermore, to estimate the film density, we analyzed real parts of the complex index of refraction (n). The values of n were computed by using a Kramers–Kronig transformation.[8] The n of film formed with charged species was $\sim$1.94, which was lower than the n value ($n=2.10$) in the film without charged species. These results suggest that the density of SiN_x films formed without charged species is higher than that with charged species, and the SiN_x films formed with charged species include voids generated by ion bombardments.

The deposition condition optimized for obtaining films near stoichiometry was as follows: total pressure of 0.5 Pa, gas flow rate of $N_2/SiH_4=100/5$ sccm, microwave power of 300 W, substrate bias of floating, and substrate temperature of 300 °C. The dielectric constant (ϵ) of films is a key factor,

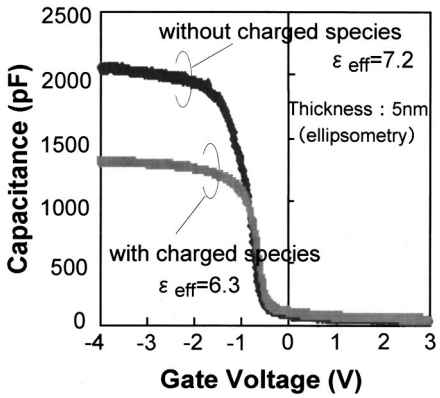


FIG. 4. Typical $C-V$ curves of MIS capacitors recorded at 0.1 MHz for SiN_x films formed with and without charged species.

because it is closely related to the thickness of the gate dielectric film in ULSI. Figure 4 shows typical $C-V$ curves, recorded at 0.1 MHz, which are corrected for series resistance effect for SiN_x films formed with and without charged species. The areas of Hg electrode with and without charged species were about 1.47×10^{-3} and 1.75×10^{-3} cm^2, respectively. The dielectric constant was calculated from the accumulated capacitance value. The ϵ of the film formed with charged species was ~6.3, whereas the ϵ was remarkably improved ($\epsilon=7.2$) without charged species, which was an almost ideal value ($\epsilon=7.5$) for Si_3N_4. These results also suggest that the density of SiN_x films formed without charged species is higher than that with charged species, and the SiN_x films formed with charged species include voids generated by ion bombardment. As for the fixed charge, the value estimated from the flatband voltage of high-frequency $C-V$ curves was low in both SiN_x films formed with and without charged species.

The leakage current between the SiN_x film and Si substrate is an important parameter for the gate dielectric film in ULSI. Figure 5 shows the curve of current density as a function of electrical field ($J-E$ curve) in the films formed with and without charged species. The areas of Hg electrode with

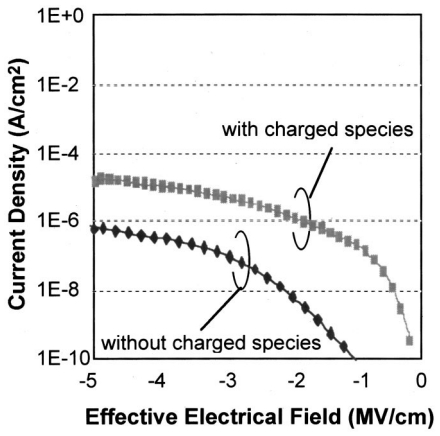
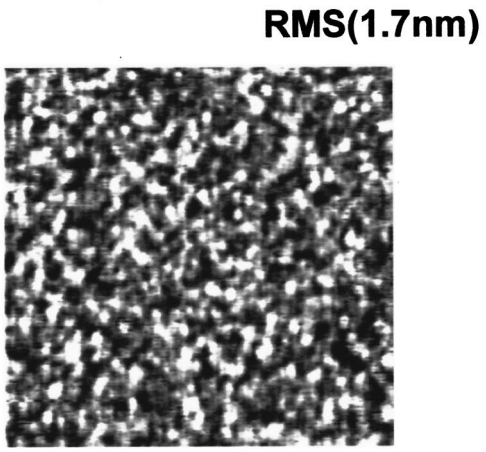


FIG. 5. Comparison of gate leakage current between SiN_x films formed with and without charged species.



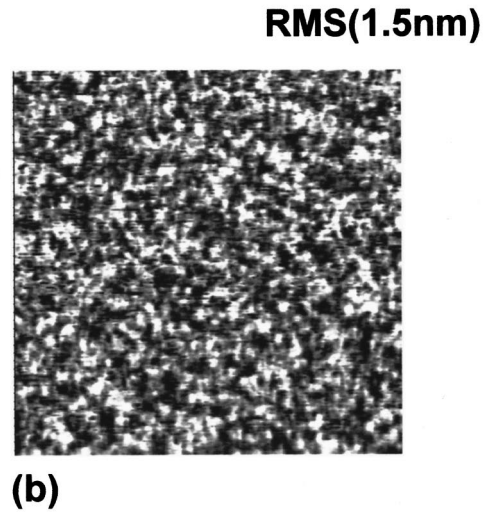


FIG. 6. *In situ* AFM images of SiN_x film surfaces formed: (a) with charged species; (b) without charged species.

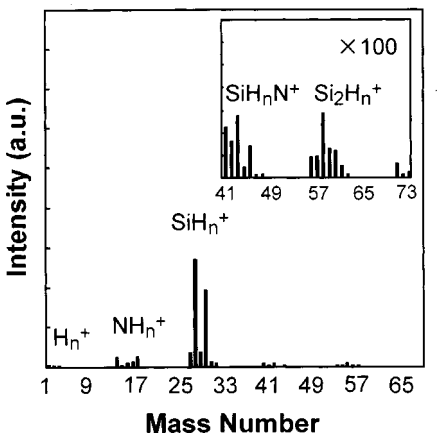


FIG. 7. Mass spectra for ECR N_2/SiH_4 PECVD operating at total pressure of 0.5 Pa, gas flow rate of $N_2/SiH_4=100/5$ sccm, microwave power of 300 W, and substrate bias of floating.

and without charged species were about 1.47×10^{-3} and 1.75×10^{-3} cm^2, respectively. The dominant current component is due to the Frenkel–Poole conduction mechanism.[9] A low leakage current is obtained in the case without charged species. At a voltage of 1.5 V, the corresponding effective electric field is about 3 MV/cm for the equivalent oxide thickness[10] of 2.5 nm. For SiN_x films formed without charged species, the current density at 3 MV/cm is 7×10^{-8} A/cm^2, which satisfies the required leakage current density of less than 2×10^{-7} A/cm^2 at the operating electric field for 256 Mbyte DRAM.

To clarify the mechanism of leakage current with and without charged species, we observed the surface roughness of films by using *in situ* AFM. Figure 6 shows AFM images of the SiN_x films formed (a) with charged species and (b) without charged species. The thickness of all films observed by AFM was 5 nm. As shown in Fig. 6, the rms surface roughness of the films formed without charged species was evaluated as about 1.5 nm, which was smoother than that of films formed with charged species, which was 1.7 nm. However, no obvious difference was observed for the surface roughness of films formed with and without charged species. These results indicate that the factor determining the leakage current between the SiN_x film and Si substrate is not due to surface roughness. However, Garcia *et al.* investigated the relationship between the composition and leakage current.[5] The film compositions were adjusted to near stoichiometry in this study. Therefore, the factor determining the leakage current is not considered to be due to the film composition. Consequently, we consider that the ion bombardment on the growth affects the leakage current in the film because the film composition is stoichiometry, and no hydrogen as a contamination and no obvious difference for the surface roughness were observed in both cases with and without charged species.

Figure 7 shows mass spectra for ECR N_2/SiH_4 PECVD in the mass/charge (m/z) range between 1 and 80. The plasma was operated at a total pressure of 0.5 Pa, gas flow rate of $N_2/SiH_4=100/5$ sccm, microwave power of 300 W, and substrate bias of floating. In QMS, there were no peaks above 100 in the m/z number. SiH_n^+ ions ($n=1$–3) at 29–31 were prominently visible. Additionally, there were peaks of SiH_nN^+ ions ($n=1$–4) at 43–46 and $Si_2H_n^+$ ions ($n=1$–5) at 57–61 and 70–72, together with NH_n^+ ions ($n=0$–2) at 56.[11,12] On the other hand, in R-CVD, we could not detect any peaks due to ions. From this result, we confirmed that charged species incident on the substrate were completely eliminated during growth in R-CVD. At this time, we cannot evaluate the effect of each ion on the surface reaction for the formation of films.

We consider that the Si_3N_4 films formed have an amorphous structure and that voids are induced in the films with charged species. Because ϵ of a void is equal to 1, it is likely that the dielectric constant of SiN_x films decreases because of voids, and the larger density of dangling bonds that line the void will cause the leakage current. As a result, the leakage current of SiN_x films formed with charged species was higher than that without charged species. Thus, the voids in the SiN_x films are successfully reduced by eliminating charged species.

Consequently, we consider that R-CVD, where the charged species in ECR-PECVD employing N_2/SiH_4 gases are eliminated by the magnetic field, has a bright future for synthesizing ultrathin gate dielectric SiN_x films with good quality at 300 °C.

IV. CONCLUSIONS

We have successfully investigated the effects of ion bombardment on the leakage current and dielectric constant of ultrathin SiN_x films formed at 300 °C, with and without charged species in ECR PECVD. By eliminating charged species, namely R-CVD, the leakage current of the SiN_x films was remarkably reduced. Furthermore, the dielectric constant of the SiN_x films was remarkably improved to be near ideal. From *in situ* FT-IR RAS spectra, we confirmed that the density of SiN_x films increased by eliminating charged species. These results suggest that the density of SiN_x films formed without charged species is higher than that with charged species, and that SiN_x films formed with charged species include voids generated by ion bombardment. As a result, the control of ion bombardment on growth was found to be a key factor for forming SiN_x films with low leakage current and high dielectric constant at low temperatures in PECVD. Thus, the R-CVD method is considered to be very useful for forming ultrathin SiN_x gate dielectric films in next-generation ULSI.

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