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Synthesis of Fluorinated SiN$_x$ Gate Dielectric Films Using ECR-PECVD Employing SiF$_4$/N$_2$/H$_2$ Gases

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1. Introduction
As device dimensions shrink below 0.1μm in ultralarge-scale integrated circuits (ULSIs), the thickness of the gate dielectric film (SiO$_2$) in FETs will fall to the 1-2 nm range. This situation leads to the large leakage due to a tunneling current in FETs. So, the dielectric film of a higher dielectric constant will replace the SiO$_2$ film. The silicon nitride (SiN$_x$) film attracts much attention as the scaled gate dielectric films in next generation ULSIs [1,2]. However, the conventional SiN$_x$ film formed at a low temperature has a poor interface with silicon and is leaky due to a high trap density in the film. Therefore, less incorporation of hydrogen and/or stabler hydrogen bonds (N-H bond energy:4.2eV) in the film are desired to improve device characteristics. Our group has investigated SiN$_x$:F films formed at a low temperature of 350°C in plasma-enhanced chemical vapor deposition (PECVD) employing NH$_3$/SiF$_4$ and found a few hydrogen atoms and Si-F bond (5.73eV) in the film improved the quality of SiN$_x$ gate dielectric films [3]. On the basis of these results, the precise control of hydrogen (H) and fluorine (F) atom concentration in the film will enable us to get excellent properties for the gate dielectric film. However, the correlation between film structures and electrical properties in SiN$_x$:F films has never been clarified. In this paper, the chemical composition and film structures of the SiN$_x$:F films have been investigated with controlling atomic ratio of films in ECR-PECVD employing SiF$_4$, N$_2$ and H$_2$ gases. The high performances of Si:N:F for the gate dielectric film have been obtained.

2. Experimental
The SiN$_x$:F films were formed by ECR-PECVD employing SiF$_4$, N$_2$ and H$_2$ gases. The conditions were as follows; a total pressure of 0.5 Pa, a microwave power of 300W, and a substrate temperature of 350°C. Microwave power excited at a frequency of 2.45 GHz was introduced through a quartz window. H$_2$ gas flow rate was varied at four conditions of 0, 10, 35 and 50sccm in a N$_2$/SiF$_4$ gas flow rate of 70/3.5sccm (ratio:20). The N/Si composition ratio in the films and electrical properties were also measured in N$_2$/SiF$_4$ gas flow rate of 70/0.7 (ratio:100) and 70/0.35 (ratio:200) conditions. SiN$_x$ films were formed on n-type (100) silicon substrates. Silicon substrates were cleaned by HF (HF:H$_2$O=1:10) solution at room temperature before deposition. The physical thickness of film was evaluated using the ratio of the Si2p bulk to chemically shifted Si2p which was calibrated by an ellipsometry in in-situ X-ray photoelectron spectroscopy (XPS) measurement. These film properties such as chemical composition and band gap, and the surface reactions for the SiN$_x$ film formation were characterized by in-situ XPS and Fourier transform infrared spectroscopy (FT-IR). The electrical properties of films were estimated by the leakage current density-voltage (J-V) and the capacitance-voltage (C-V) characteristics curve.

3. Results and Discussion
The charge transfer from Si to the more electronegative F leaves a positive charge on the Si atom, which results in a shift of Si core levels towards higher binding energy in XPS. The peak shift (3.1eV) of fluorinated SiN$_x$ film was higher than that of conventional SiN$_x$ film (2.6eV). In addition, the peak shifts of fluorinated SiN$_x$ films were increased linearly with increasing F concentration in films. The binding energy shifts of the N1s level were independent of the fluorine concentration. These facts suggest that Si-H$_x$ bonds were replaced by Si-F$_x$ bonds, and N-F$_x$ bonds do not exist at all in the fluorinated SiN$_x$ films.

Figure 1 shows the F concentration and the normalized absorption intensity of Si-N bonds as a function of H$_2$ flow rate. With increasing the H$_2$ flow rate, the F concentration decreased. These results indicate that hydrogens scavenge the surplus fluorines in the films. The addition of hydrogens makes the following effects on the kinetics of F atoms, 1) the gas-phase reaction: F+H$_2$→HF+H and 2) the surface

![Fig.1 In-situ XPS and FT-IR results of F concentration and normalized absorption intensity of Si-N$_x$ bonds as a function of H$_2$ flow rate.](image-url)
reaction: F+H→HF in SiF₄ plasmas. F atoms play an important role in the termination of Si dangling bonds. However, large amounts of F concentration cause a decrease of dielectric constant or contribute to etching of SiNₓ films. By changing H₂ flow rate, it was found that the F concentration in the film was successfully controlled. On the other hand, the normalized absorption intensity of Si-N bonds increased with increasing the H₂ flow rate. These results show that films are densified with increasing the H₂ flow rate. As shown in Fig.2, the energy bandgap (Eg) was determined by using N₁s energy loss spectra of XPS [4]. The Eg of SiNₓ:F film (5.4±0.1eV) estimated was approaching to the near value of bulk SiNₓ film (4.75eV), with increasing the H₂ flow rate. This result also supports the fact that films are densified.

Figure 3 shows the N/Si composition ratio in the SiNₓ:F films. It was found that the composition of film was varied from Si-rich composition to N-rich one with increasing the H₂ flow rate and N₂ dilution ratio. The N/Si ratio of near the ideal stoichiometry can be attained by controlling H₂ flow rate and N₂ dilution ratio. From these results, hydrogens contribute to the etching of Si-Si bonds and extracting reaction of Si-F bonds, and thus Si-N bonds are formed in films by inserting reaction with N atoms which were increased by high dilution of N₂. These reactions have enhanced the film densified. The dielectric constant was above about 6.0 which was also controlled by N/Si ratio in the film.

Figure 4 shows C-V and J-V characteristics as a function of N₂ dilution ratio. These results exhibit that with increasing the N₂ dilution ratio, the hysteresis attributed to charge trap densities did not exist and the excellent hysteresis loop (0mV) was achieved. This fact means the electrical traps in SiNₓ:F films are negligible. Furthermore, the SiNₓ:F formed with high N₂ dilution (N₂/SiF₄=200) was found to have the excellent leakage current which was low by several orders of magnitude compared to that with low N₂ dilution (N₂/SiF₄=20).

4. Conclusion

We have synthesized ultrathin SiNₓ:F films of 4nm in thickness on a Si substrate at low temperature of 350℃ in ECR-PECVD employing SiF₄/N₂/H₂ gases. The ultrathin SiNₓ:F film was evaluated as a gate dielectric film, and was found to have a very low leakage current and an excellent hysteresis loop (0mV). In-situ XPS and FT-IR observations indicated that the large N₂ dilution for the proper quantity of H₂ were very effective for forming the Si-Nₓ network. Consequently, highly densified SiNₓ:F film was successfully synthesized, which is one of the most promising material for ultrathin gate dielectric films in next generation ULSIs.

References