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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℃ in plasma-enhanced chemical vapor deposition (PECVD) employing NH_3/SiF_4 and found the fewer 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 precious 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 SiN: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℃. 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 ($HF:H_2O$=1:10) solution at room temperature before deposition. The physical thickness of film was evaluated using the ratio of the Si2*p* bulk to chemically shifted Si2*p* 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: $F+H_2 \rightarrow HF+H$ and 2) the surface

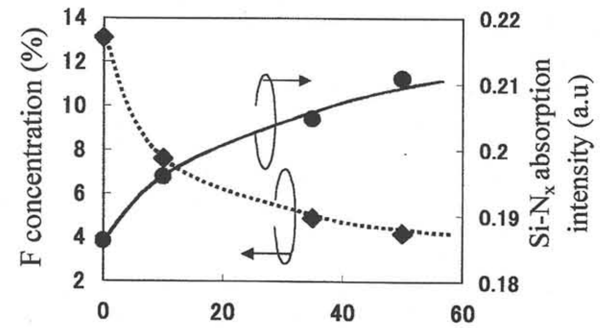

Fig.1 *In-situ* XPS and FT-IR results of F concentration and normalized absorption intensity of Si-N_x bonds as a function of H_2 flow rate.

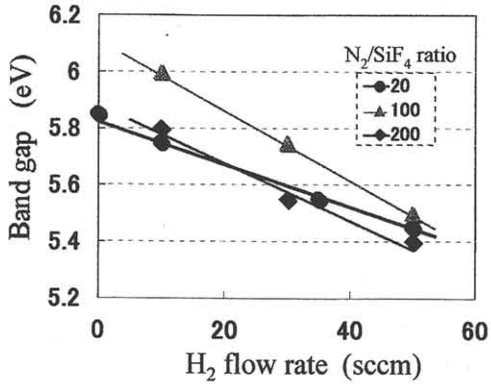

Fig.2 The energy bandgap (Eg) by using N1*s* energy loss spectra of XPS as a function of H_2 flow rate and of N_2/SiF_4 ratio (20, 100 and 200).

reaction: F+H→HF in SiF_4 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 SiN_x films. By changing H_2 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 H_2 flow rate. These results show that films are densified with increasing the H_2 flow rate. As shown in Fig.2, the energy bandgap (Eg) was determined by using N1*s* energy loss spectra of XPS [4]. The Eg of SiN_x:F film (5.4±0.1eV) estimated was approaching to the near value of bulk Si_3N_4 film (4.75eV), with increasing the H_2 flow rate. This result also supports the fact that films are densified.

Figure 3 shows the N/Si composition ratio in the SiN_x:F films. It was found that the composition of film was varied from Si-rich composition to N-rich one with increasing the H_2 flow rate and N_2 dilution ratio. The N/Si ratio of near the ideal stoichiometry can be attained by controlling H_2 flow rate and N_2 dilution ratio. From these results, hydrogens contribute to the etching of Si-Si bonds

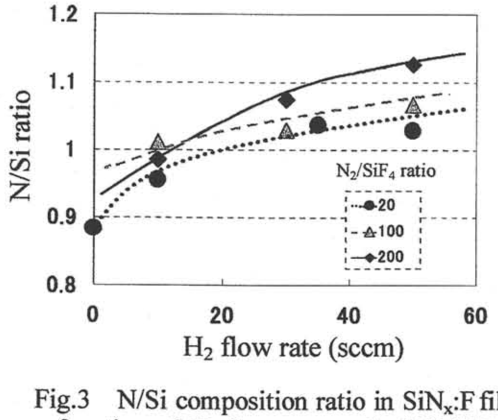

Fig.3 N/Si composition ratio in SiN_x:F film as a function of H_2 flow rate and of N_2/SiF_4 ratio (20, 100 and 200).

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 N_2. 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 N_2 dilution ratio. These results exhibit that with increasing the N_2 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 SiN_x:F films are negligible. Furthermore, the SiN_x:F formed with high N_2 dilution (N_2/SiF_4=200) was found to have the excellent leakage current which was low by several orders of magnitude compared to that with low N_2 dilution (N_2/SiF_4=20).

4. Conclusion

We have synthesized ultrathin SiN_x:F films of 4nm in thickness on a Si substrate at low temperature of 350℃ in ECR-PECVD employing $SiF_4/N_2/H_2$ gases. The ultrathin SiN_x: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 N_2 dilution for the proper quantity of H_2 were very effective for forming the Si-N_x network. Consequently, highly densified SiN_x:F film was successfully synthesized, which is one of the most promising material for ultrathin gate dielectric films in next generation ULSIs.

References

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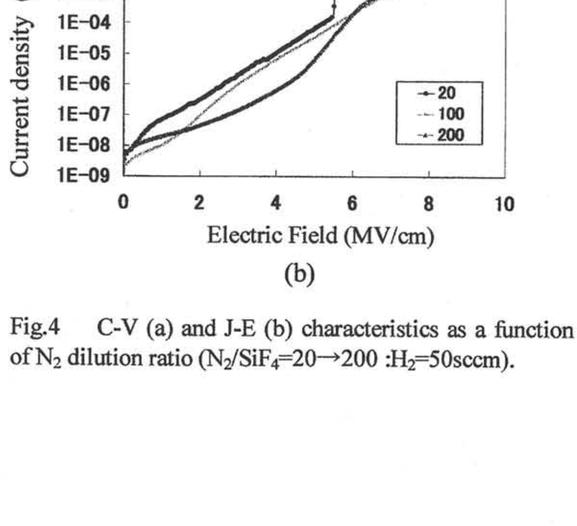

Fig.4 C-V (a) and J-E (b) characteristics as a function of N_2 dilution ratio (N_2/SiF_4=20→200 :H_2=50sccm).