Extended Abstracts of the 2000 International Conference on Solid State Devices and Materials, Sendai, 2000, pp. 180–181

A-5-3

Ultrathin Fluorinated Silicon Nitride Gate Dielectric Films Formed by Plasma Enhanced Chemical Vapor Deposition Employing NH_3 and SiF_4

Hiroyuki Ohta, Atsushi Nagashima, Masaru Hori and Toshio Goto.

Department of Quantum Engineering, Graduate School of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
(Phone/FAX: +81-52-789-4420, E-mail: kxc02410@niftyserve.or.jp)

1.Introduction

The silicon nitride (SiN_x) film attracts much attention as scaled gate dielectric films in next generation's ULSI[1]. However, the conventional SiN_x film has a poor interface with silicon and is leaky due to a high trap density in the film.

Recently, we have developed ultrathin fluorinated SiN_x films formed by ECR-PECVD employing NH_3/SiF_4. It is known that the average bond energy (5.73eV) of Si-F is higher than that of Si-H (3.18eV)[2]. Therefore, it is expected that the Si-F bond in the film should have improved the quality of gate dielectric film.

In this study, we have investigated properties of ultrathin SiN_x films (4nm) formed at 350℃. This film (fluorinated SiN_x films) contains fewer hydrogen atoms than the conventional SiN_x films formed by ECR-PECVD employing NH_3/SiH_4. This fluorinated SiN_x film reduced successfully the leakage current by several orders of magnitude than the thermal SiO_2 in the identical EOT. These film properties and the surface reactions for the SiN_x film formation with good quality are discussed on the basis of results of the *in-situ* XPS, *in-situ* FT-IR RAS, FT-IR, GDS and TDS.

2.Experimental

Figure 1 shows a schematic diagram of the experimental apparatus of typical ECR-PECVD system with a divergence magnetic field used in this study[3]. SiN_x films were formed on n-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.

In this system, the process chamber is equipped with *in-situ* FT-IR RAS. The FT-IR RAS has been applied for *in-situ* observation of the growth process of SiN_x films under ECR-PECVD conditions employing NH_3/SiH_4 and NH_3/SiF_4. Furthermore, the XPS system is connected to the ECR-PECVD chamber through a transfer chamber in a vacuum.

The electrical properties of the SiN_x films were evaluated with making an $Al/SiN_x/Si$ diode structures of electrode area of 3.98mm^2. In these samples, no post metal annealing treatments were performed. The leakage current density-voltage (J-V) characteristics were measured by using a semiconductor parameter analyzer (Hewlett-Packard : 4156B).

3.Results and Discussion

Figure 2 shows the leakage currents measured in SiN_x films formed employing NH_3/SiH_4, NH_3/SiF_4 and the conventional thermal SiO_2 films whose equivalent oxide thickness (EOT) is about 2.8nm[4]. It was found that the leakage currents were drastically decreased by employing NH_3/SiF_4. Particularly, J-V characteristics exhibit the minimum leakage current in NH_3/SiF_4 (50/20sccm). The fluorinated SiN_x film formed by NH_3/SiF_4 reduced the leakage current by several orders of magnitude than the thermal SiO_2 in the identical EOT.

Figure 3 shows FT-IR RAS results of normalized absorption intensity of Si-N bonds and fluorine concentration determined from *in-situ* XPS, as a function of SiF_4 flow rate. With increasing the SiF_4 flow rate, the normalized absorption intensity of Si-N bonds decreased and the fluorine concentration had the tendency of saturation at flow rates above 20sccm. These results suggest that surplus fluorines contribute to etching of SiN_x films. The conditions of NH_3/SiH_4 PECVD were optimized for obtaining near stoichiometry. The typical condition in NH_3/SiF_4 PECVD was as follows; a total pressure : 0.5Pa, gas flow rate : NH_3/SiF_4=50/20sccm, a microwave power : 300W, a substrate bias : floating, a substrate temperature : 350℃.

Figure 4 show C-V curve of (a) SiN_x film formed employing NH_3/SiH_4 and (b) fluorinated SiN_x film formed employing NH_3/SiF_4. There were the hump and hysteresis (0.04V) attributed to charge traps in the SiN_x film observed in C-V data of SiN_x films formed employing NH_3/SiH_4. On the other hand, the hump was not observed in C-V data of fluorinated SiN_x films formed employing NH_3/SiF_4 and the excellent hysteresis (0.02V) was achieved with employing NH_3/SiF_4. These results suggest that the state trapping density of SiN_x films formed employing NH_3/SiF_4 is much lower than that employing NH_3/SiH_4. The dielectric constant of both SiN_x films were almost the same value. We considered that these value were dependent on the composition of SiN_x films. N/Si ratio of fluorinated SiN_x films was about 0.95 (Si-rich).

Figure 5 shows the FT-IR spectra of (a) SiN_x film formed employing NH_3/SiH_4 and (b) fluorinated SiN_x film formed employing NH_3/SiF_4, which exhibit the Si-N bonds. The hydrogen concentration of as-deposited fluorinated SiN_x film, as evaluated by the N-H and Si-H signals, is low as compared to the SiN_x film formed employing NH_3/SiH_4. Furthermore, the hydrogen concentration was determined from glow discharge spectroscopy (GDS) (Rigaku : GDS3870) and indicated the similar tendency of FT-IR results.

Figure 6 shows the thermal desorption mass spectroscopy (TDS) of fluorinated SiN_x film formed employing NH_3/SiF_4. The amount of desorption gas of H_2 was observed above 350℃. However, F and F_2

were not observed. This fact suggests that fluorine bonds in fluorinated SiN_x film are stable.

4.Conclusion

We have clarified effects of fluorines in the SiN_x films for improvement of MIS characteristics. As a result, the control of fluorine concentration in the SiN_x films was found to be a key factor for forming the fluorinated SiN_x films with high quality at low temperatures. No hump, excellent hysteresis and low leakage currents were achieved in MIS with fluorinated SiN_x films formed employing NH_3/SiF_4 (50/20sccm). The fluorinated SiN_x is very effective for ultrathin gate dielectric films in next generation's ULSI.

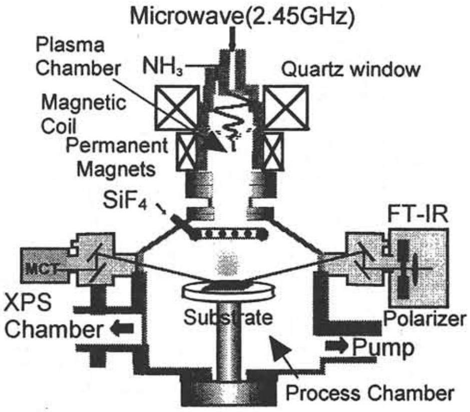

Fig.1 Schematic diagram of the experimental apparatus of typical ECR-PECVD system.

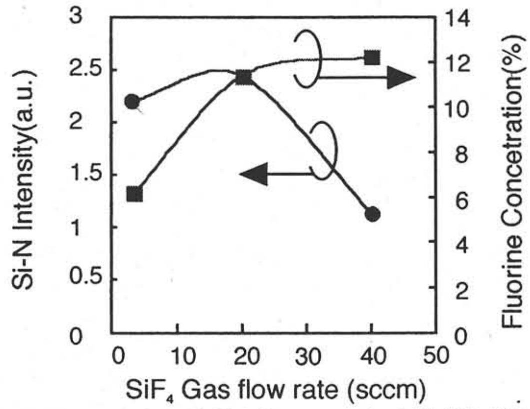

Fig.2 J-V characteristics with SiN_x films employing NH_3/SiH_4, NH_3/SiF_4(50/3, 50/20, 50/40sccm) and the conventional thermal SiO_2.

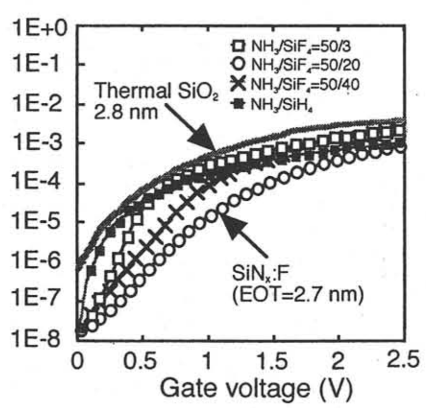

Fig.3 FT-IR RAS results of normalized absorption intensity of Si-N bonds and fluorine concentration, as a function of SiF_4 flow rate.

Acknowledgments

We would like to thank Dr. S. Fukuyama at Fujitsu Laboratory and N. Yamashita at Rigaku Industrial Corporation for TDS and GDS measurements.

References

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

[2] P. J. Wright, et al, IEEE Trans. Electron Devices, 45, p.879,(1989)

[3] H. Ohta, et al, Ext. Abst. of SSDM., p.156, (1999)

[4] T. P. Ma, IEEE Trans. Electron Devices, **45**, p.680, (1998)

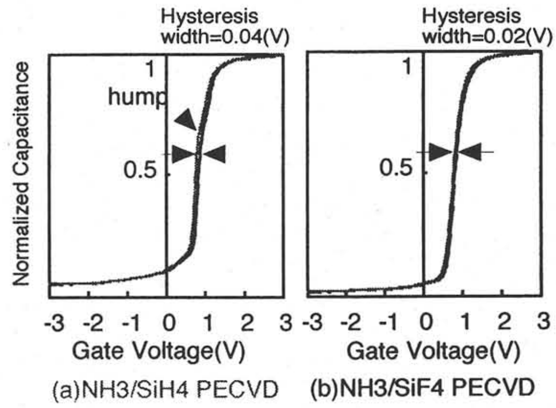

Fig.4 C-V curve of (a) SiN_x film formed employing NH_3/SiH_4 and (b) fluorinated SiN_x film formed employing NH_3/SiF_4.

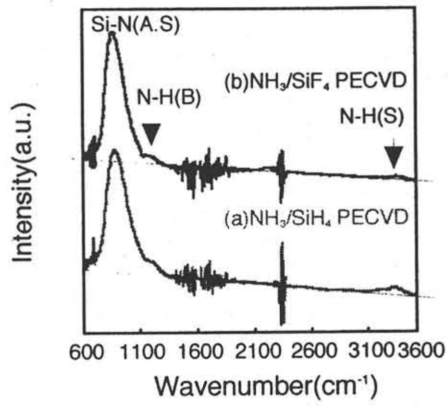

Fig.5 FT-IR spectra of (a) SiN_x film formed employing NH_3/SiH_4 and (b) fluorinated SiN_x film formed employing NH_3/SiF_4.

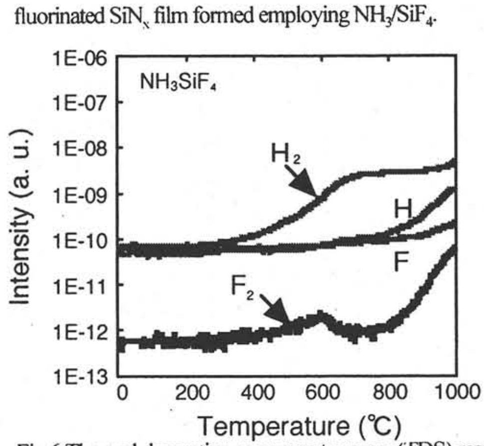

Fig.6 Thermal desorption mass spectroscopy (TDS) results of fluorinated SiN_x film formed employing NH_3/SiF_4.