Extended Abstracts of the 1999 International Conference on Solid State Devices and Materials, Tokyo, 1999, pp. 500-501

B-12-3

PE-CVD of Thermally Stable Low-k IMD Films Using Low-GWPC_5F_8

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1. Introduction

Shrinkage of the metal-line spacing in ultra large scale integrated circuits requires low dielectric constant intermetal dielectric (IMD) films for reducing resistivity-capacitance time delay. For the feature dimensions less than 0.13 μm, IMDs have to have the dielectric constant below 2.5[1]. Amorphous fluorinated carbon (a-C:F) films deposited by plasma enhanced chemical vapor deposition (PE-CVD) methods are promising candidates for the IMDs, and the process integration using a-C:F has been successfully demonstrated by Endoh *et al.* However, the most commonly used source gas is C_4F_8, and it possesses quite high global warming potential (GWP) of 8,700 and atmospheric life time of 3,200 years[2]. Therefore, substitutional gases possessing lower GWP and life time are required from the view point of environmental protection. Recently, C_5F_8, which have GWP and life time as low as 100 and 1 year, has been introduced to the reactive etching processes[2]. In this paper, C_5F_8 is applied for an IMD film deposition process, and the properties of the films, especially their thermal stability, are reported. Gas-phase of the plasma is also investigated for explaining the film properties.

2. Experimental

Schematic representation of the experimental setup were reported elsewhere[3]. Films were deposited on (100) p^+-type Si substrates using a capacitively coupled RF (13.56 MHz) PE-CVD reactor. The diameter of the RF electrode and the distance between the electrode and grounded substrate holder were 70 and 30 mm, respectively. The diameter of the substrate holder is the same as the RF electrode.

Although C_5F_8 is liquid source at room temperature (25°C), its vapor pressure is as high as approximately 560 mmHg. Therefore, C_5F_8 was supplied to the reaction chamber through a mass flow controller without bubbling by any inert gases. Summary of the deposition conditions is listed in **Table I**.

The thermal stability of the films was investigated by measuring the infrared (IR) absorption intensity at the wavenumber of 1000-1500 cm^{-1}, which corresponds to C-F$_n$ (n=1,2, and 3) bonds in the films, as a function of annealing temperature. The thermal treatment was performed for 1 hour in N_2 ambient at 1 atm. The dielectric constant of the films was determined by measuring the capacitance of a metal-insulator-semiconductor (MIS) structure consisting of Al, film and p^+-Si at the frequency of 1 MHz. Gas phase of C_5F_8 plasma was investigated by optical emission spectroscopy (OES).

Table I. Film deposition condition

Substrate temperature	50, 100, 200, 300°C
RF power	40 W
Pressure	0.2 Torr
C_5F_8 flow rate	3.2, 16 sccm
C_4F_8 flow rate	3.2, 16 sccm

3. Results and Discussion

Figure 1 shows deposition rate of the films as a function of substrate temperature for the C_5F_8 flow rate of 3.2 and 16 sccm. While the deposition rate decreases down to zero at 300°C for the flow rate of 3.2 sccm, it keeps 80 nm/min at 300°C for the flow rate of 16 sccm. Deposition rate for C_4F_8 plasma, which is shown in the same figure for comparison, is fairly low in comparison to that for C_5F_8 plasma. In order to increase the deposition rate, hydrogen or hydrocarbon gases are required[4]. However, the use of H-containing gases increases dielectric constant of the films. Therefore, the high deposition rate at elevated temperature is another advantage of C_5F_8 in addition to its original feature of low GWP.

Figure 2 shows the dielectric constant of the films prepared from 16 sccm C_5F_8. The films prepared at 100, 200 and 300°C show the dielectric constant less than 2.0 of poly-TFE films. The films prepared at elevated temperature is usually considered to have a rigid structure, which results in higher density and higher dielectric constant. Our results show opposite characteristics. At this moment, we cannot explain the cause of this characteristics. Presumably, the films prepared at higher temperature might have porous structure due to desorption of a part of film components.

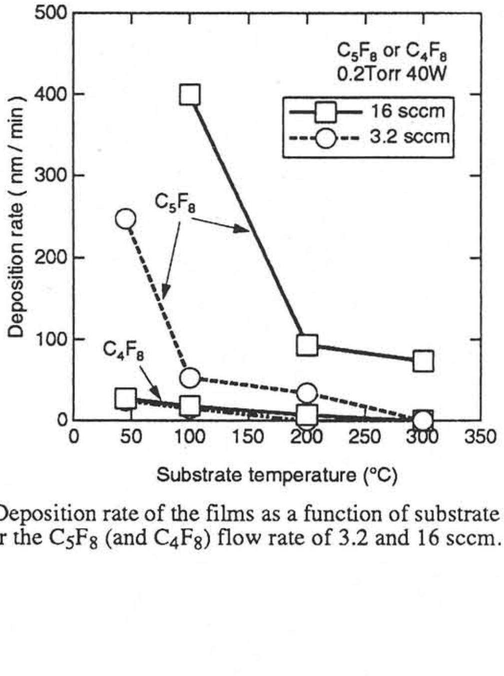

Fig.1 Deposition rate of the films as a function of substrate temperature for the C_5F_8 (and C_4F_8) flow rate of 3.2 and 16 sccm.

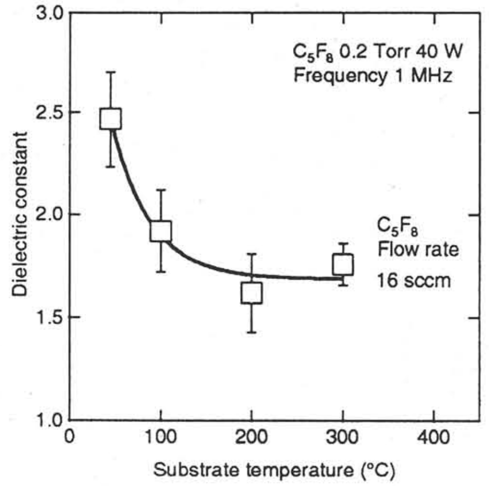

Fig.2 Dielectric constant of the films prepared from C_5F_8 as a function of substrate temperature for the flow rate of 16 sccm. The measurements were performed at the frequency of 1 MHz.

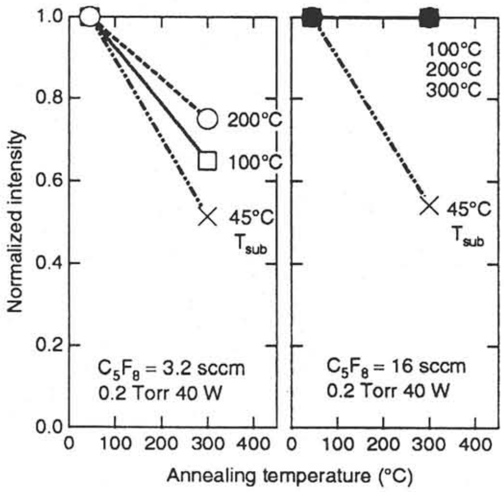

Fig.3 Thermal stability of the films prepared from C_5F_8 as a funciton of substrate temperature for the flow rate of 3.2 (a) and 16 sccm (b). Annealing of the films was performed for 1 hour in nitrogen ambient.

Figure 3(a) and **3(b)** show thermal stability of the films prepared under the C_5F_8 flow rate of 3.2 and 16 sccm. In this figure, decrease of the intensity by annealing means thermal instability of the films.

As seen in **Fig.3(a)**, the films prepared from low flow rate of 3.2 sccm show poor thermal stability although the stability improved by increasing substrate temperature. On the other hand, as seen in **Fig.3(b)**, the films prepared from 16 sccm of C_5F_8 show excellent stability, except for the film deposited at 45°C. The thickness of the films, which is not shown in this paper, also did not change for these stable films. From these results, it is concluded that the films prepared from higher flow rate show higher thermal stability.

Figures 4(a) and **4(b)** show the OES spectra of the plasma under the flow rate of 3.2 and 16 sccm. As seen in the figure, there is a marked difference between the two spectra. The spectral profile for 3.2 sccm is similar to CF_4 plasma, while that for 16 sccm has large peak corresponding to CF_2* and CF_2^+. Therefore, it is suggested that large contribution of CF_2 might be realized under the high flow rate, and which has improved thermal stability of the films. This phenomenon must have relationships to the mean residence time in the reaction chamber and frequency of secondary reactions in the gas phase.

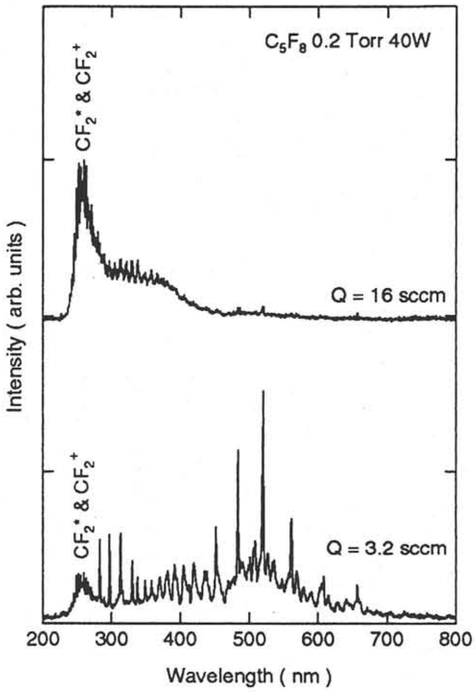

Fig.4 OES spectra of the C_5F_8 plasma under the flow rate of 3.2 and 16 sccm. Measurements were performed 17 and 24 seconds after turning RF power on, respectively.

4. Conclusion

In conclusion, low-*k* a-C:F films have been prepared from low-GWP source of C_5F_8 by a PE-CVD method, and it has been found that the films prepared under higher flow rate of C_5F_8 shows higher thermal stability in addition to higher deposition rate. This result suggests that importance of control of secondary reactions by means of adjusting the mean residence time of gas phase species in the reaction chamber.

Acknowledgments

This work has been partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, and the Kinki-Area Invention Center.

References

[1] T. Horiuchi: Proc. 20th Symp. Dry Process (Inst. Elec. Eng. Japan, Tokyo, 1998), p.163.
[2] Y. Ito, A. Koshiishi, R. Shimizu, M. Hagiwara, K. Inazawa and E. Nishimura: Proc. 20th Symp. Dry Process (Inst. Elec. Eng. Japan, Tokyo, 1998), p.263.
[3] T. Shirafuji, Y. Nakagami, Y. Hayashi and S. Nishino: Plasma and Polym., **3** (1998), 115.
[4] S. Takeishi, H. Kudo, R. Shinohara, M. Hoshino, S. Fukuyama, J. Yamaguchi and M. Yamada: J. Electrochem. Soc. **144** (1997) p.1797.