

Plasma Diagnosis of Remote PECVD for SiOCH Deposition at Low Temperature

Yuji Yoshizako, Daisuke Tsukiyama, Daisuke Nakamura, Keisuke Yamaoka,
Yoshikazu Terai and Yasufumi Fujiwara

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University,
2-1 Yamadaoka, Suita, Osaka 565-0871, JAPAN
Fax: +81-6-6879-7536, e-mail: y-terai@mat.eng.osaka-u.ac.jp

The plasma characteristics of a remote plasma enhanced chemical vapor deposition system for low-temperature deposition using tetraethoxysilane (TEOS) have been investigated. In Langmuir probe measurements in Ar gas, the plasma density was controlled by radio frequency (RF) power and a spacing length between a plasma chamber and a reactor chamber at the low density of $10^9 \sim 10^{10} \text{ cm}^{-3}$. During the film deposition, the substrate temperature increased with RF power, but the low-temperature deposition at 30°C was achieved at the RF power of 50 W. The deposition rate of the films strongly depended on RF power. Fourier transform infrared measurements showed that SiOCH films with higher carbon composition were grown at lower RF power. The RF power-dependence of the deposition rate and the carbon composition was understood by the dissociation and desorption of hydrocarbons (C_mH_n) in TEOS precursors. Key words: PECVD, TEOS, SiOCH film, low temperature deposition

1. INTRODUCTION

Carbon-doped silicon oxide (SiOCH) is one of the insulators in electronic devices due to their low leakage current, low dielectric constant ($k < 3$) and high thermal stability. The deposition requires a low-temperature process ($< 400^\circ\text{C}$) since any subsequent high-temperature process may destroy the devices. The SiOCH films have been deposited by plasma-enhanced chemical vapor deposition (PECVD) below 400°C using various organosilicon sources, such as tetramethylsilane [1] and tetramethylcyclotetrasiloxane [2]. In the PECVD of SiO_2 for very-large-scale-integrated (VLSI) circuits, tetraethoxysilane [$\text{Si}(\text{OC}_2\text{H}_5)_4$: TEOS] has been widely used because it can produce void-free, conformal filling over fine features [3,4]. The electron impact and an substrate temperature of $\sim 200^\circ\text{C}$ can enhance the dissociation of hydrocarbons (C_mH_n) from TEOS precursors, result in the deposition of carbon-free silicon oxide [5,6]. In our recent study [7], however, we have succeeded in the low-temperature deposition of SiOCH films by a remote PECVD using TEOS and pointed out that the combination of low plasma density and low substrate temperature enables the SiOCH deposition with high carbon composition and low leakage current of $\sim 10^{-7} \text{ A/cm}^2$ at 0.5 MV/cm . The SiOCH films are considered to be very porous due to their high etching rate and low refractive index.

In this paper, we present the results of a plasma diagnosis in the remote PECVD by Langmuir probe measurements. The effects of plasma density and the substrate temperature on the film properties were investigated systematically.

2. EXPERIMENT

Figure 1 shows a schematic of the remote PECVD system in which plasma generation and film formation are spatially separated. In the plasma chamber, capacitively-coupled plasma (CCP) was generated by a

radio frequency (RF) generator of 13.56 MHz connected to cylindrical electrodes. In the reactor chamber, a substrate holder was placed far from the plasma chamber and was electrically grounded. The distance (L) between the substrate holder and the center of plasma was variable by changing a spacing tube placed under the plasma chamber. In this study, the distance was fixed at $L = 275$ or 375 mm to keep plasma-density and substrate-temperature low. The plasma diagnosis in Ar gas without TEOS was performed by a single type of Langmuir probe method. The probe was a cylindrical tantalum wire, $5 \times 10^{-2} \text{ cm}$ in diameter and was 1.5 cm in length. Plasma parameters of ion density, space potential and the electron temperature were obtained by analyzing the current-voltage (I_p - V_p) characteristic curve at the center of the substrate holder. In a

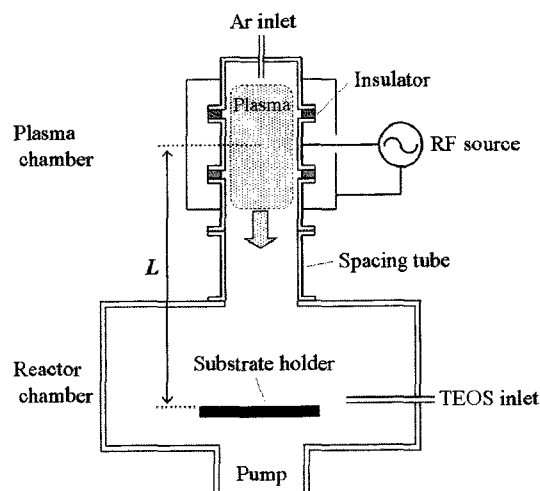


Fig. 1. Schematic of the remote plasma enhanced chemical vapor deposition (PECVD) system.

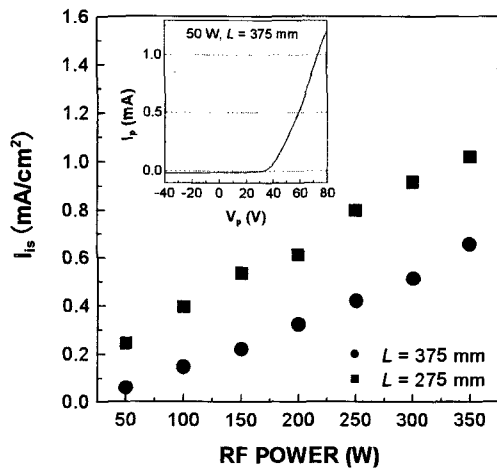


Fig. 2. Dependence of ion saturation current (I_{is}) on RF power. The inset is a typical I_p-V_p curve measured at 50 W, $L = 375$ mm.

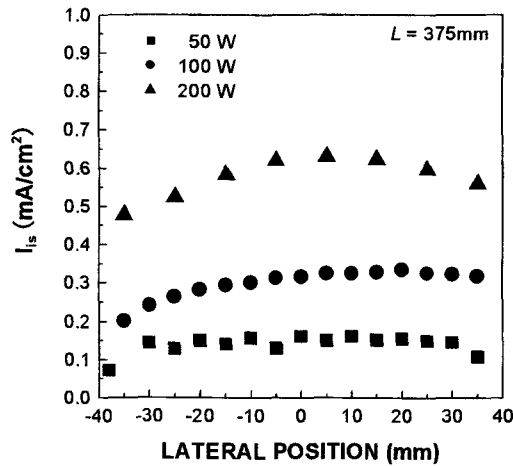


Fig. 3. Lateral distribution of ion saturation current (I_{is}) at the position of the substrate holder.

TEOS/Ar mixture, we could not perform detail experiments for the deposition of oxides on the tantalum probe tip. The variation of the substrate temperature under different plasma conditions was measured by clamping a type-K thermocouple to the substrate holder.

The films were deposited on *n*-type Si(100) substrates without intentional heating and cooling. A TEOS cylinder was kept at 40°C and a flow rate was fixed at 1.0 sccm. During the deposition, a mixture of Ar gas and TEOS was introduced into the chambers through a heated inlet. The flow rate of Ar gas was 3.5 sccm. The flow rates of TEOS and Ar were controlled by using mass flow controllers. Total pressure during the film deposition was about 20 Pa in the reactor chamber. The input RF power was changed in the range of 50–300 W. The Ar plasma is effective to suppress the dissociation of hydrocarbons which exist in the gas-phase as well as on the substrate surface [8]. The deposition time was fixed at 90 min. The thickness and refractive index of the deposited films were measured by

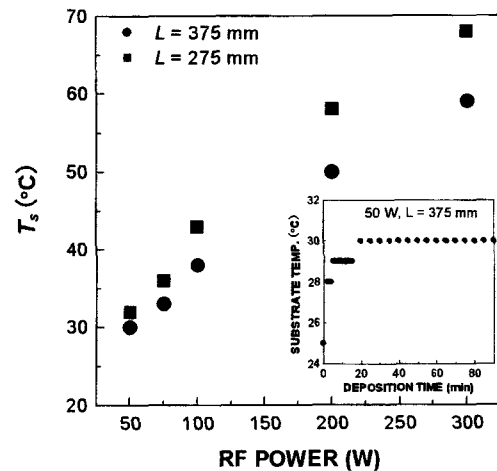


Fig. 4. Saturated substrate temperature (T_s) as a function of RF power. The inset shows the variation of the substrate temperature with time.

ellipsometry. The composition of the films was investigated by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) measurements.

3. RESULTS AND DISCUSSION

Figure 2 shows the results of the current–voltage measurements in Ar gas of 3.5 sccm without TEOS. The inset of Fig. 2 is a typical I_p-V_p curve measured at 50 W, $L = 375$ mm. From the I_p-V_p curves, we obtained ion saturation current (I_{is}), electron temperature (kT_e) and space potential (V_s) at different RF powers. As seen in the figure, I_{is} increases with the increase of RF power and shows larger value at $L = 275$ mm. kT_e and V_s become small with RF power in the range of 1.5–3 eV and 10–50 V, respectively. The plasma density ranges from 4×10^9 cm⁻³ at 50 W to 3×10^{10} cm⁻³ at 350 W in the condition of $L = 375$ mm. These results indicate that we can control the ion saturation current (plasma density) by RF power and the distance between the plasma center and the substrate holder. In a diagnosis in O₂ and TEOS/O₂ plasma [9], it has been reported that the ion density in TEOS/O₂ plasma became smaller than that in O₂ plasma. Therefore, we could not define the plasma density in the TEOS/Ar mixture, but the RF power-dependence must be the same in both cases. Figure 3 shows the lateral distribution of the ion saturation current along the substrate holder at different RF powers. The lateral position zero corresponds to the center of the substrate holder. At the RF power of 50 W, the ion saturation current is almost constant. With increasing RF power, the distribution of the ion saturation current has a peak at the center position. The nonuniform profiles reflect the characteristics of diffusion-dominated plasmas. The lateral distribution of kT_e and V_s is constant at any RF power. The results indicate that the Ar plasma generated in the plasma chamber is uniformly carried to the substrate holder with the size of 60×60 mm. The uniformity of the plasma is supported by the result that the fluctuation of the film thickness is smaller than 2% in the 30-mm diameter.

The inset of Fig. 4 shows the substrate temperature

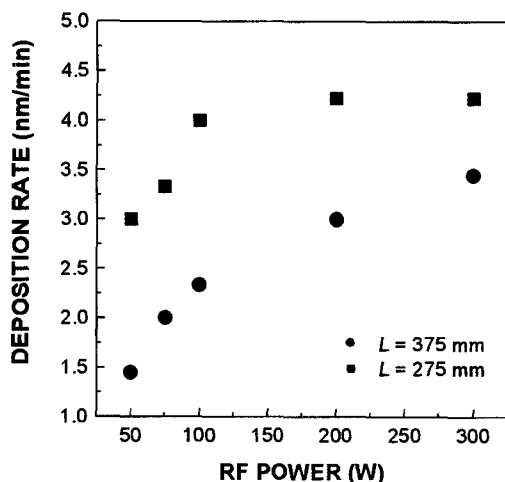


Fig. 5. Deposition rate of SiOCH films as a function of RF power at TEOS (1.0 sccm) + Ar (3.5 sccm).

variation with time during the film deposition at 50 W, $L = 375$ mm. When the plasma is generated, the substrate temperature rises rapidly, and then it is saturated after 20 min. The saturated substrate temperature (T_s) is plotted in the main part of Fig. 4. T_s rises with increasing RF power from 30°C to 70°C, presumably due to increased plasma ion bombardment. This result convinces us that the low-temperature deposition at 30°C is achieved at the RF power of 50 W.

Figure 5 shows the deposition rate of the films as a function of RF power. At $L = 375$ mm, the deposition rate increases from 1.4 nm/min at 50 W to 3.4 nm/min at 300 W. The rates at $L = 275$ mm are much larger than that of $L = 375$ mm. In both lengths, however, the rate is saturated at higher RF power. The RF-dependence of the deposition rate is different from that of I_{ts} in Fig. 2.

The inset of Fig. 6 shows FT-IR spectra of the film deposited at 50 W, $L = 375$ mm. The small absorption peaks are observed at 2935 and 2976 cm^{-1} . These absorption peaks are CH_2 and CH_3 stretches in the ethoxy ($\text{O}-\text{C}_2\text{H}_5$) groups of the TEOS molecules [6, 10]. Details of the identification have been described in Ref. [7]. The largest absorbance band centered at about 1070 cm^{-1} is from Si-O-Si stretching [10]. The result shows the formation of Carbon-doped silicon oxide. The carbon composition of the SiOCH film is estimated to $\text{SiO}_{1.53}\text{C}_{0.87}\text{H}$ by XPS measurements [7]. We obtained the integrated intensity of the CH_n and Si-O-Si absorbance and plotted the ratio of $\text{CH}_n/\text{Si-O-Si}$ in the main part of Fig. 6. The films deposited at low RF power shows the large $\text{CH}_n/\text{Si-O-Si}$ ratio. The ratio decreases rapidly as RF power increases. The result shows that the SiOCH films with higher carbon composition can be deposited at lower RF power. The RF power-dependence of carbon content in FT-IR corresponds to the results of the quantitative analysis by XPS measurements [7]. The carbon composition and the RF power-dependence are almost same in $L = 275$ mm and $L = 375$ mm.

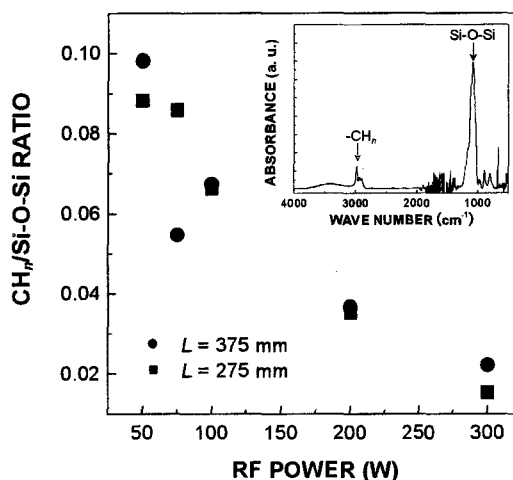
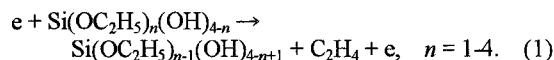


Fig. 6. Integrated intensity ratio of CH_n and Si-O-Si absorbance as a function of RF power. The inset shows a FT-IR spectra of the film deposited at 50 W, $L = 375$ mm.

The deposition rate of the film by PECVD using TEOS + Ar depends on two critical factors: the generation rate of TEOS precursors in the gas phase, and the adsorption/desorption rate of the precursors on the sample surface. The gas phase reaction of TEOS in the reactor chamber can be described as [5]



The electron impact decomposes the TEOS molecule, resulting in the formation of the precursors. The reaction occurs more frequently and the dissociation of hydrocarbon of C_2H_4 is enhanced at higher RF power because the ion current (plasma density) is larger at high RF power (in Fig. 1). In addition, the desorption rate of the precursors is enhanced at higher RF power due to the increase of the substrate temperature in Fig. 4. In fact, the desorption of the hydrocarbons on the sample surface is much enhanced at the low substrate temperature of 45-100°C [6]. Therefore, the decrease of the carbon composition at higher RF power in Fig. 6 is understood by the enhanced dissociation and the desorption of hydrocarbons during the deposition.

The dependence of the deposition rate on RF power in Fig. 5 is explained as follows. The density of the TEOS precursors in the gas phase is proportional to the ion saturation current (plasma density). The higher deposition rate at $L = 275$ mm is due to the larger ion saturation current than $L = 375$ mm. However, the deposition rate is saturated at high RF power though the ion current becomes large with increasing RF power. In carbon-doped silicon oxide, it is known that steric hindrance of the hydrocarbons produces nanovoids in the films and decreases the dielectric constant [11]. In other words, the incorporation of the hydrocarbons in the silicon oxide can reduce the film density. In our experiments, the SiOCH films deposited at low RF power shows lower refractive index than that deposited at high RF power [7]. The result shows that the film

density becomes large by the enhanced dissociation and the desorption of hydrocarbons at high RF power. Therefore, the saturation of the deposition rate at high RF power is considered to be due to the variation of the film density.

4. CONCLUSION

We have measured the plasma properties of the remote PECVD for the low-temperature deposition of SiOCH by Langmuir probe experiments. The ion saturation current is controlled by input RF power and the spacing tube between the plasma chamber and the reactor chamber at low plasma density of $10^9\text{--}10^{10}\text{ cm}^{-3}$. The low-temperature deposition below 60°C is confirmed by the measurements of saturated substrate temperatures at 50-300 W. We succeeded in the low-temperature deposition of $\text{SiO}_{1.53}\text{C}_{0.87}\text{H}$ by the remote PECVD using TEOS/Ar. The combination of the low plasma density and the low substrate temperature is effective to the deposition of SiOCH films with high carbon composition. The RF power-dependence of the deposition rate and the carbon composition is understood by the enhanced dissociation and the desorption of hydrocarbons during the deposition.

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REFERENCES

- [1] A. Grill and V. Patel, *J. Appl. Phys.* **85**, 3314-3318 (1999).
- [2] A. Grill, *J. Appl. Phys.* **93**, 1785-1790 (2003).
- [3] C. S. Pai and C.-P. Chang, *J. Appl. Phys.* **68**, 793-801 (1990).
- [4] C.-P. Chang, C. S. Pai and J. J. Hsieh, *J. Appl. Phys.* **67**, 2119-2126 (1990).
- [5] M. A. Lieberman and A. J. Lichtenberg, "Principles of Plasma Discharges and Materials Processing", Wiley-Interscience, New York (1994) pp. 518-521.
- [6] S. C. Deshmukh and E. S. Aydil, *J. Vac. Sci. Technol. B* **14**, 738-743 (1996).
- [7] K. Yamaoka, Y. Yoshizako, H. Kato, D. Tsukiyama, Y. Terai and Y. Fujiwara, *Physica B*, *in press*.
- [8] S. Wickramanayaka, A. Matsumoto, Y. Nakanishi, N. Hosokawa, Y. Hatanaka, *Jpn. J. Appl. Phys.* **33**, 3520-3527 (1994).
- [9] F. Nicolazo, A. Goulet, A. Granier, C. Vallée, G. Turban and B. Grolleau, *Surf. Coat. Technol.* **98**, 1578-1583 (1998).
- [10] S. P. Mukherjee and P. E. Evans, *Thin Solid Films* **14**, 105-118 (1972).
- [11] R. S. Brusa, M. Spagolla, G. P. Karwasz, A. Zecca, G. Ottaviani, F. Corni, M. Bacchetta and E. Carollo, *J. Appl. Phys.* **95**, 2348-2354 (2004).

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