# Formation of electrical conductive hard-carbon (DLC) films using i-$C_4H_{10}/N_2$ supermagnetron plasma

Haruhisa Kinoshita, Jun Takahashi, Takuya Hando

*Research Institute ofElectronics, Shizuoka University3-5-1 Johoku, Hamamatsu 432-8011, Japan*

Electrical conductive hard-carbon (DLC) films were formed by using a supennagnetron plasma CVD method. Using mixed gas ofisobutane (i-$C_4H_{10}$) and N , DLC films were deposited on thermally oxidized Si wafers, and film deposition rate, hardness and resistivity were measured. Two rf powers of the same frequency (13.56 MHz) with rf phase difference of 180° were supplied to each electrode. The lowest resistivity of 1.7xl0³ cm was observed at N concentration of 70%, gas pressure of 50 mTon; electrode temperature of 80°C, and rf powers of 900 W/ 900W. In this case, measured film deposition rate and hardness were 2300Å/*min* and 1700 kg/mm², respectively.

## 1. Introduction

Hard-carbon, i.e. diamond-like carbon (DLC), films have been formed by several methods such as ion beam deposition', laser ablation deposition², plasma CVD (chemical vapor deposition)[3, 4] To enhance the deposition rate in plasma CVD, the utilization of high density plasma is effective. Magnetron , ECR³, and inductively coupled (ICP) plasmas are typical high density plasmas used for semiconductor IC processings. Supermagnetron plasma has been also used for high throughput plasma etching[7,8] and plasma CVD[4,9], because of its high plasma density. Electrically conductive DLC films doped with nitrogen have been formed by CH /N supermagnetron plasma CVD[4]. Electrically conductive films have been studied for the formation of field emission devices, and threshold voltages were observed to decrease by lowering the io resistivity10.

In this study, we used isobutane (i-$C_4$ $H_{10}$) instead of $CH_4$ as a source gas to enhance the deposition rate. i-$C_4H_{10}$ includes four carbon atoms in one molecule, therefore deposition rate is expected to increase comparing with the case of $CH_4$. Resistivity, hardness, deposition rate were measured as functions of parameters such as $N_2$ concentration, electrode spacing, electrode temperature, gas pressure and rf powers supplied to upper and lower electrodes.

## 2. Experimental details

Figure 1 shows the supermagnetron plasma CVD apparatus with two parallel electrodes. Two rfpowers of the same rf frequency (13.56 MHz) were supplied to each electrode. Phase difference between two rf voltages was controlled to be about 180" by using a phase-shifter to obtain maximum deposition rate.4 A magnetic field of about 80 G was applied along the electrodes using an annular permanent magnet magnetized in the cross- diameter direction.' A si wafer covered with a $SiO_2$ layer (0.7 µm thickness) was put on a lower electrode keeping good thermal conductivity between them using a diffusion pump oil. The lower electrode was cooled or heated to 10 – 80°C during deposition using a water circulator. This Si wafer was introduced into the CVD chamber through a load-lock chamber (LLC) without breaking the vacuum. The upper electrode was covered with a graphite plate to avoid the contamination of a wafer by sputtering of upper metal electrode. The electrode spacing was controlled to be 20 - 60 mm. i-$C_4H_{10}$ and $N_2$ were introduced into the CVD chamber through two mass flow controllers. Resistivity and hardness were measured using four-point probe tester and microhardness tester, respectively.

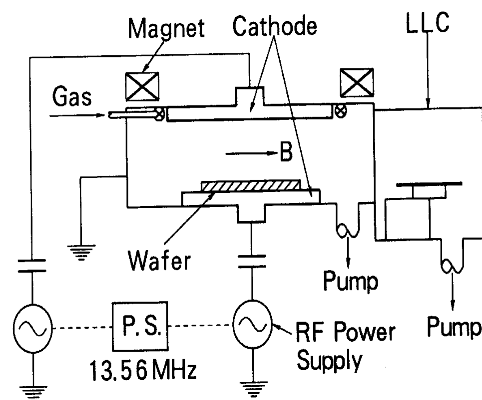


Fig. 1. Schematic of the supermagnetron plasma CVD apparatus with a load-lock chamber.

## 3. Results and discussion

DLC films could be formed up to the thickness of about 2.4 µm without peeling off from wafers naturally. To measure the film resistivity, all of the films were formed to the thickness of about 1.2 µm by adjusting the deposition time.

Figure 2 shows the $N_2$ concentration dependencies of three film parameters (resistivity, hardness and deposition rate). In this experiment, flow rate of i-$C_4H_{10}$ was fixed to 50 sccm and the flow rate of $N_2$ versus total gas flow rate was increased from 0 to 80%. Upper and lower electrode

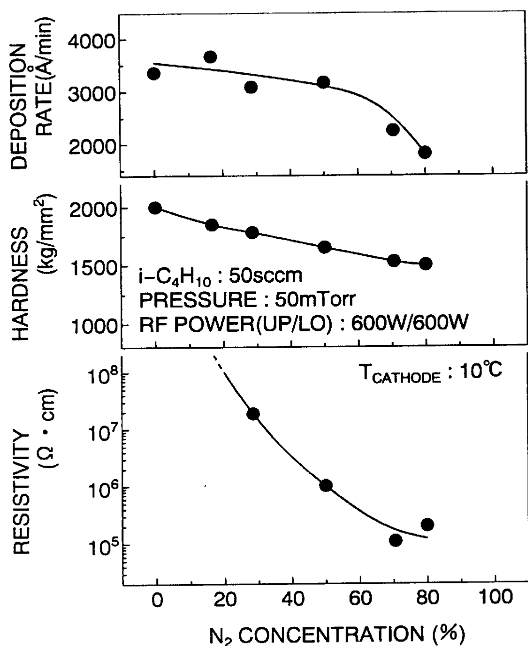


Fig. 2. $N_2$ concentration dependence ofresistivty, hardness and deposition rate.

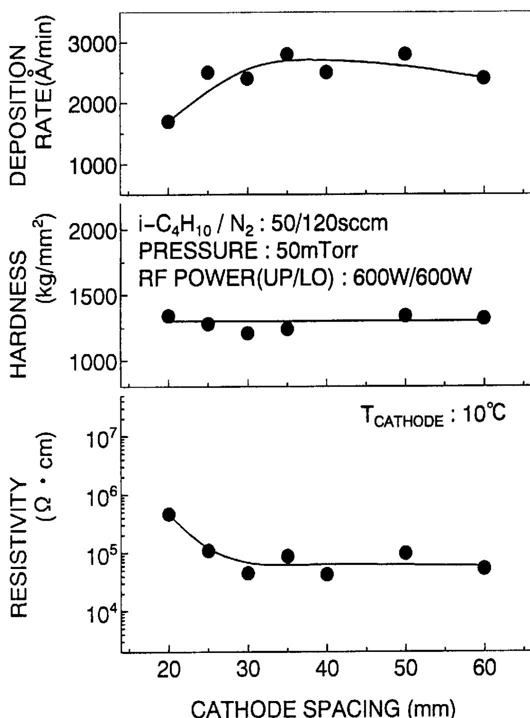


Fig. 3. Electrode spacing dependence of resistivty, hardness and deposition rate.

rf powers (UPRF and LORF) were 600W/600W. Lower electrode temperature was 10°C and electrode spacing was 40mm. In the $N_2$ concentration of 10%, film resistivity was higher than an order of 10'0   cm, i.e. this film is an insulator. Film hardness was 2000 kg/mm2, and it was higher than the hardness of glass (1340KG/mm$^2$). Deposition rate was about 3500 Å/*min,* and it was higher than the deposition rate (about 1500 Å/*min)* of film formed by $CH_4/N_2$ supermagnetron plasma.[4] By the increase of carbon atoms included in one molecule, deposition rate would be increased. With increase of $N_2$ concentration, resistivity decreased rapidly to an order of $10^5$   cm. Hardness and deposition rate decreased a little with increase of $N_2$ concentration. With further increase of $N_2$ concentration more than 70%, deposition rate decreased rapidly. Therefore, we selected the best $N_2$ concentration of 70% to obtain low resistivity films.

Three film parameters were measured as a function of electrode (cathode) spacing, as shown in Fig.3. In the spacing of 30 - 60 mm, three parameters changed little, i.e. resistivity of about 6x104   cm, hardness of about 1300 kg/mm$^2$, deposition rate of 2700 Å/*min.* At the spacing of 20 mm, resistivity increased largely. To obtain lower resistivity film, we selected the best electrode spacing to be 40 mm.

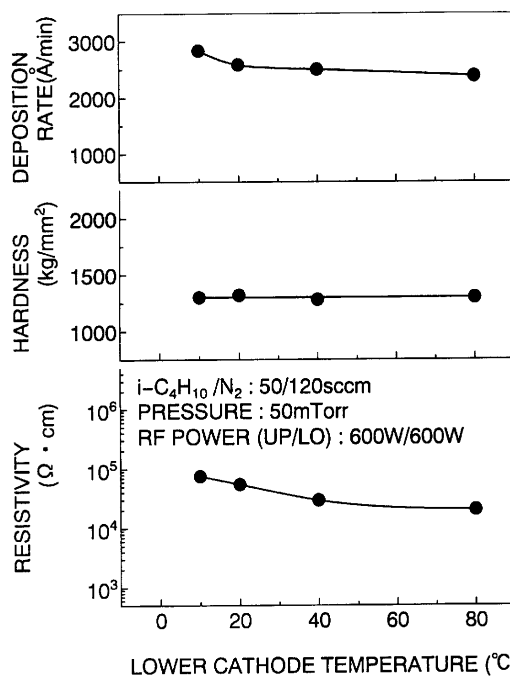


Fig. 4. Lower electrode temperature dependence of resistivity, hardness and deposition rate.

Figure 4 shows the lower electrode temperature dependencies of three film parameters. With increase of lower electrode temperature from 10 to 80°C, resistivity decreased largely. The deposition rates decreased a little, but they were higher than 2400 *Å/min.* Hardness was almost unchanged. From this experiment, decrement of resistivity was dependent largely on the wafer (lower electrode) temperature. To decrease the film resistivity, enhancement of lower electrode temperature is essential.

Gas pressure dependencies of three parameters were measured at the lower electrode temperatures of 10 and 80°C as shown in Fig.5. Deposition rate and hardness increased with gas pressure at the electrode temperatures of 10 and 80°C. Resistivity was almost unchanged with

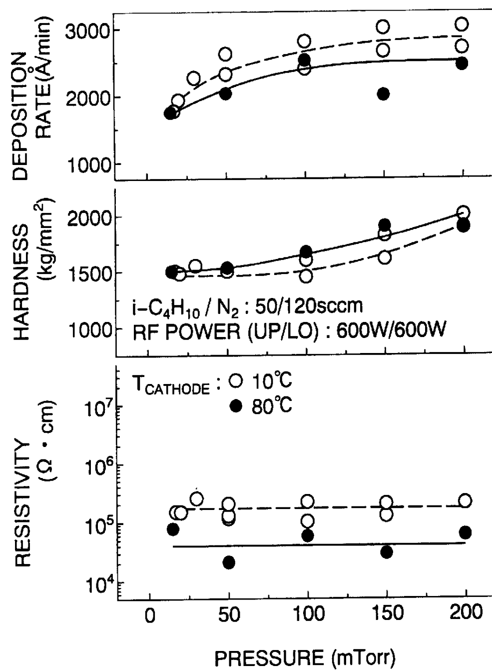


Fig. 5. Gas pressure dependence of resistivity, hardness and deposition rate.

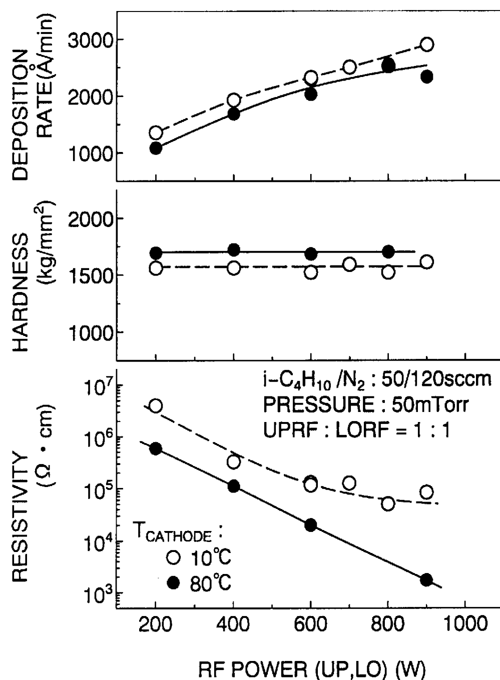


Fig. 6. Rf power dependence of resistivity, hardness and deposition rate.

increase of gas pressure. Between the gas pressure of 15and 200 mTorr, deposition rates and resistivities at 8°C were lower than those at 10°C and hardnesses at 80°C were Similar to those at 10°C. About the film resistivity, all the resistivity measured at 80°C were lower than those measured at 10°C, at the gas pressure of 15 - 200 mTorr. From this experiment, it was found that the enhancement of gas pressure is essential to increase the film hardness. Three parameters were measured as a function of rf powers (UPRF and LORF) at lower electrode temperatures of 10°C and 80°C,as shown in *Fig.6.* Rf powers were always selected to 1:1 (UPRF:LORF) at the region of 200(/200) - 900W(/900W). With increase of rf power from 200W to 900W, film deposition rate increased from about 1200 *Å/min* to about 2500 Ä/*min.* In all of rf powers, deposition rates at electrode temperature of 10°C were higher than those at 80°C Film hardnesses were almost unchanged (about 1600 kg/mm$^2$) with increase of rf powers. Film resistivity was decreased drastically with increase of rf power from 200W to 900W. In the case of lower electrode temperature of 80°C, resistivity of 200W was 6x105 cm and that of 900W was as low as 1.7x103 cm. At lower electrode temperature of 10°C, all resistivities were higher than those of 80°C. From this experiment it was found that film resistivity was largely dependent on the wafer (electrode) temperature, and the resistivity decreased drastically with increase of rf powers.

## 4. Conclusion

Electrical conductive DLC films were formed by using i-$C_4H_{10}/N_2$ supermagnetron plasma. By using i-$C_4H_{10}$ as source gas, deposition rate increased largely comparing with that of $CH_4$ source gas. The larger value of deposition rate became over 3000 Å/*min.* Hardnesses of all samples were over 1300kg/mm. Hardness increased by gas pressure increment. Film resistivity decreased with increase of wafer (electrode) temperature. Drastic decrease of resistivity was observed by increase of rf powers. The lowest resistivity of 1.7x103 *cm* was obtained at rf power of 900W.

## Acknowledgments

This study is supported in part by the Grant-in-Aid for Scientific Research (C), No.09650382 from the Ministry of Education, Science, Sports and Culture of Japan.

## References

[1] T.Mori, Y.Namba, J.Appl.Phys. **55**, 3276 (1984).

[2] F.Xiong, Y.Y.Wang, V.Leppert, R.P.H.Chang, J.Mater.Res. **8**, 2265 (1993).

[3] D.H.Kang, S.C.Ha, K.B.Kim, S.H.Min, J.Vac.Sci. Technol.A **16**, 2625 (1998).

[4] H.Kinoshita, A.Yamauchi, J.Vac.Sci.Technol.A **14**, 1933 (1996).

[5] H.Kinoshita, T.Ishida, S.Ohno, J.Appl.Phys. **62**, 4269 (1987).

[6] J.HOPWOOd, C.R.Guamieri, S.J.Whitehair, J.J.Cuomo, J.Vac.Sci.Technol. **A 11**, 152 (1993).

[7] H.Kinoshita, K.Nomoto, J.Vac.Sci.Technol.**A 10**, 1092 (1992).

[8] Kinoshita, A.Yamauchi, M. Sawai, J.Vac. Sci.Technol.B **17**, 109 (1999).

[9] H.Kinoshita, S.Nomura, M.Honda, J.Vac. Sci.Technol.A. (to be published).

[10] I.T.Han, N.Lee, S.W.Lee, S.H.Kim, D.Leon, J.Vac.Sci. Technol.B **16**, 2052 (1998).