Effects of Substrate Refrigeration on Plasma Polymerization with Fluorocarbons

Kikuko Yoshimura¹⁾, Takeshi Minaguchi¹⁾, Hirohiko Nakano¹⁾, Toshiaki Tatsuta¹⁾, Osamu Tsuji¹⁾,
Keiko Toyozawa²⁾, Takeshi Abe²⁾, and Zempachi Ogumi²⁾

¹⁾ Samco International Inc.

36, Waraya-cho, Takeda, Fuhimi-ku, Kyoto 612-8443, Japan

²⁾ Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering,
Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Effects of refrigeration of substrates during plasma polymerization were investigated with some fluorocarbons. The refrigeration of a substrate stage which worked also as a lower electrode in a plasma reactor changed the phases, gas-liquid-solid, in the reactor *in vacuo* the same as under normal atmospheric pressure in the case of hexafluoropropene (HFP). The radiofrequency power which was appropriate for yielding a solid polymer was 20–50 W at 230 °K in plasma polymerization of HFP, although the RF power was confined to about 10 W at 300 °K. Deposition rates of these polymers were about 180 Å/min and 225 Å/min, respectively. X-ray photoelectron spectroscopy spectra showed that the reaction proceeded in the presence of a liquid phase HFP. Plasma copolymerization of trifluoromethanesulfonic acid (TFMS), octafluorocyclobutane (OFCB), H₂O and HFP was carried out in the temperature range of 250–270 °K. The deposition rate and the electrical conductivity were 220 Å/min and $4.3 \times 10^{-7} \sim 3.3 \times 10^{-5}$ S/cm, respectively, while the same measurements of the copolymer obtained in the range of 300–310 °K were 7 Å/min and $2.4 \times 10^{-9} \sim 6.1 \times 10^{-6}$ S/cm. The former included more F atoms than the latter, and it suggested that the plasma ablation and excessive crosslinking were suppressed. The effects seemed to be derived from differences in the plasma activities between the monomers, and the differences were yielded by their different phase, namely, solids of TFMS and H₂O, a gas of HFP, and an alternation of a liquid and a gas of OFCB.

Key words: Plasma Polymerization with a Refrigerated Substrate, Plasma Multi-Phase Polymerization, Fluorocarbons

1. Introduction

On the basis of behavior within the plasma discharge area, organic compounds are classified into two groups, namely, materials that efficiently conduct polymerization and materials that produce primarily ablation effects. The former is applied in some industrial fields as a monomer of polymer deposition and the latter as an etching or cleaning gas. In the case of fluorocarbons, only materials having an unsaturated

bond can be applied to polymerization; the other fluorocarbons are hardly usable for such a purpose.

On the other hand, plasma polymerization of organic monomers is usually carried out at ambient temperature or above. It is known that the reactions in the gas phase greatly contribute to polymerization although the various active species are yielded not only in the gas phase, but also in the surface layer of the solid substrate and the boundary area between the gas-solid

Fig. 1. Chemical structures of fluorocarbon monomers.

phases [1]. It has also been noted that the active species yielded in the liquid phase play an important role in plasma-initiated polymerization [1].

The above knowledge suggests possibilities of a new technique, "plasma multi-phase polymerization." In other words, some monomer materials having a certain difference in boiling point (b.p.) or melting point (m.p.) can be modified to have desirable phases by changing the temperature and it is also possible that the plasma activation level may be controlled at a certain temperature even if they are within the same discharge area. There is another advantage that the difference in activity permits extended selection of the monomers, because the temperature reduction can suppress an ablation function of several compounds or can concentrate some materials, that involve an important functional group, near the surface of the substrate.

This paper reports an attempt of refrigeration of a substrate for plasma polymerization and an application of the temperature reduction to the above-mentioned technique. The three fluorocarbons shown in Fig. 1 were used as monomers. Hexafluoropropene (HFP) was employed in the basic study and was applied as a source material of polymerization in a multi-phase system. Octafluorocyclobutane (OFCB) and trifluoromethanesulfonic acid (TFMS) were used for preparation of an ion-exchange membrane by means of "plasma multi-phase polymerization." Such a membrane as is derived from fluorocarbons and contains a sulfonic group has been expected to function as a Solid Polymer Electrolyte (SPE) membrane in a variety of electrochemical systems, for example, proton-conductive electrolyte membrane fuel cells [2-5]. OFCB was a source of polymerization, being used with HFP. TFMS was a source of a functional group for cation-exchange, *i.e.*, sulfonic group.

2. Method

2-1. Materials

HFP and OFCB were supplied from Showa Denko Co., Ltd. and Kanto Denka Kogyo Co., Ltd., respectively. TFMS was purchased from Wako Pure Chemical Industries, Ltd. and Nacalai Tesque Inc. and was of the extrapure reagent grade. The H_2SO_4 for measurement of electrical conductivity was of the analytical reagent grade and was supplied by Wako Pure Chemical Industries, Ltd. A glass plate, a Si wafer, Al foil, and a porous polymer membrane were used as substrates for the plasma deposition. The Celgard® 2500 (CG) of Hoechst Celanese Corporation was made from polypropylene and polyethylene resins and had an average pore size of $0.19 \times 0.05 \mu\text{m}^2$. The Duragard® 3401 (DG) was a product of Polyplastics Co. and was polypropylene membrane which was treated for hydrophilicity and had an average pore size of $0.20 \times 0.03 \mu\text{m}^2$. Water was used after deionization.

2-2. Plasma Reactor System

A Plasma Deposition System Model PD-10 (Samco International Inc.) as illustrated in Fig.2 was employed for the research. It was equipped with a High Vacuum Pump E2M-18 (300 l/min, Edwards Inc.), a Signal Generator Model 8647A (250 kHz~1000 MHz, Hewlett Packard Inc), a Radiofrequency (RF) Power Amplifier Model A150 (ENI Inc.), and a Cryo Mini Refrigerator (Iwatani Cryo-Techno Corporation Inc.) incorporated into a Thermo-controller Model TCU-3 (Iwatani Gas Inc.). Two thermostats (Thermo Electric DR61, Komatsu Electronics Inc.) were equipped for vaporization of liquid monomers.

The stainless steel bell jar ($\phi 32 \text{ cm} \times \text{H } 34 \text{ cm}$) in which the temperature was controlled at 30°C was evacuated from the bottom via a liquid nitrogen cold trap and the pressure was monitored with a Pirani

Fig. 2. Schematic diagram of plasma reactor system.

Gauge GP-1SRY (ULVAC Japan Ltd.). The reactor was internally installed with a pair of parallel electrodes (2.5 cm [HFP] or 3.0 cm [TFMS-OFCH-HFP] in gap). The upper electrode (ϕ 10 cm) was drum-shaped and was drilled to open some nozzles at the lower side. The lower electrode (ϕ 12 cm) had a role of a substrate stage and its temperature can be varied between 30 and 310° K. RF electric power of 13.56 MHz was supplied from the generator to the electrodes via a power meter and a matching network. The monomers other than TFMS were supplied through mass flow controllers (MFC, Estec Inc.). The TFMS was evaporated under reduced pressure, transported into the upper electrode, and diffused downward from the nozzles onto the lower electrode.

2.3 Plasma Polymerization Procedure

The substrates were put on the lower electrode after the surface cleaning: the surface cleaning was processed by wiping with acetone for glass, Si and Al and by air-blown for CG and DG. The reactor was then evacuated down to a pressure below 5.0 Pa. A cleaning gas was introduced into the reactor and the pressure was equilibrated. The plasma excitation was initiated and sustained by supplying the RF power. The reactor was deeply evacuated again and the plasma polymerization was performed on the substrate to form a thin film by the same manner as the above-mentioned plasma cleaning.

The plasma cleaning was carried out with 10 sccm (cm^3/min under STP) of Ar at 10 W of RF power for about 1 minute and the monomer gas was introduced after the refrigeration of the lower electrode in the case

of simple plasma polymerization of HFP. In the case of plasma copolymerization of HFP, OFCB, H_2O and TFMS, the plasma cleaning was carried out with 5 sccm of H_2O for 2 minutes and the monomer gases were introduced before the refrigeration in order to monitor the flow rate of the liquid monomers, i.e. H_2O and TFMS, by changes of the pressure.

All operative conditions were determined so as to obtain a solid polymer film most efficiently and uniformly.

2.4. Evaluation of Plasma Polymer

The deposition rate of the plasma polymer was calculated from the film thickness and the reaction time. The thickness was measured with a Surface Profile Measuring System Dektak 3030 and Dektak³ST (ULVAC Japan Ltd.) by tracing a step formed at the boundary position between the polymer film and the bare surface of the substrate (glass or Si). The bare surface was provided by removing a cover glass or a piece of Si wafer placed on the substrate before the plasma polymerization. X-ray photoelectron spectroscopy (XPS) spectra were obtained from the polymer deposited on Al, CG, and DG employing a Shimadzu ESCA-3200 (Shimadzu Inc.). Relative ratios of atom numbers were calculated from the peak areas of the XPS spectra (C_{1s} , F_{1s} , S_{2p} , O_{1s}). The electrical conductivity of the polymer was determined by use of a Potentiostat/Galvanostat HA-501 (Hokuto Denko Co.), in which two Pt wire terminals and two Ag/AgCl electrodes were incorporated. The polymer-deposited CG or DG was held vertically between a pair of glass cells having a 0.7 cm^2 circular hole on each of

their attached sides. Both attached cells were filled with 0.5 mol/L H_2SO_4 aqueous solution and the Pt terminal together with the Ag/AgCl electrode were inserted into the two cells. An ohmic resistance of the sample was obtained from a potential difference between the solutions by sending various electric currents to the terminals.

3. Results and Discussion

3.1. Plasma Polymerization of HFP with a Refrigerated Substrate

Matter often differs in behavior between normal atmospheric pressure and reduced pressure. The effects of the refrigeration of the lower electrode on the monomer gas were investigated with HFP. The pressure at 2.5 sccm of HFP in the reactor was measured *in vacuo* with a decrease or an increase in the

temperature of the lower electrode. The results are shown in Fig.3. While HFP has m.p. at 117.0°K and b.p. at 243.8°K , Fig. 3 indicates that the change of the state of HFP depends not upon the pressure of the reactor but upon the temperature of the electrode. An abrupt change appeared at a temperature close to the m.p., but an insignificant change appeared near the b.p. especially when the temperature was increased. The observation of the lower electrode agreed with the change of the pressure. White frost appeared or disappeared on the electrode at the m.p. and varnish-like gloss also at the b.p. These results suggest that change of the temperature brought about fusion and coagulation at the m.p. and condensation and vaporization at the b.p. in spite of the reduced pressure of the reactor. Fig. 3 also shows that sublimation pressure of HFP is much lower than the vapor pressure and therefore the

(A) Decrease in temperature.

HFP: 2.5 sccm ; preparatory vacuum: 310°K , 3.0 Pa.

(B) Increase in temperature.

HFP: 2.5 sccm ; preparatory vacuum: 319°K , 3.0 Pa
 $\rightarrow 99^\circ\text{K}$, 3.0 Pa $\rightarrow 30^\circ\text{K}$, 0.4 Pa.

Fig. 3. Pressure of HFP at various temperatures of substrate stage.

Fig. 4. Effects of refrigeration of substrate on plasma deposition rate of PPHFP.
 HFP: 2.5 sccm ; pressure: 10 Pa ; substrate: Si wafer.

significant increase in pressure occurred near the m.p. of HFP.

The plasma polymerization of HFP on a refrigerated substrate was carried out at 230 °K that is a temperature at which HFP is liquid and easy to be vaporized. An attempt at a much lower temperature than 230 °K resulted in insufficient polymerization and yielded oligomer oil. The deposition rate of plasma-polymerized HFP (PPHFP) at 230 °K was compared with that at 300 °K in Fig. 4. Although the plot of deposition rate vs. RF power at 230 °K was 60-85 Å/min higher than that at 300 °K over the range of RF power 5-35 W, their profiles were similar to each other. However, the deposition rate at 300 °K was reduced in contrast to the rate at 230 °K as the RF power increased towards 50 W. With regard to the properties of the membrane such as mechanical strength, the HFP prepared at 35 W was brittle. It was supposed, therefore, that plasma ablation strengthened competition against polymerization at 35 W or above at ambient temperature. The PPHFP prepared at 10 W at 300 °K was good and those prepared in the range of 20-50 W at 230 °K showed similar quality. The deposition rate of the former was 225 Å/min and those of the latter were about 180 Å/min.

Fig. 5 shows the XPS spectra of C_{1s} obtained from

PPHFP prepared under the same operative condition that was applied to the previous experiment. The spectra at 35 W and at 50 W prepared at 230 °K were similar to those at 10-20 W and 20-35 W prepared at 300 °K, respectively. The results implied that the energy supplied as RF power was consumed as thermal and kinetic energy therefore the polymerization at 230 °K had need of more RF power than that at 300 °K in order to yield the polymer which was equal in elemental composition and chemical structure. Another characteristic of the XPS spectra of PPHFP prepared at 230 °K is that the spectra determined without Ar ion etching had a close resemblance to those determined after 120 s of etching in the range of 10-20 W. It was suggested that HFP preserved in liquid phase was well polymerized and convection of HFP adhering on the surface of the substrate occurred efficiently during the reaction.

The presumption was in good agreement with a supposition obtained from Fig.6 in which the ratios of atom numbers of PPHFP prepared at various RF powers. The F/C represents a degree of crosslinking and preservation of the chemical structure of the monomer. The O/C exhibited incorporation of oxygen derived from the air remaining in the reactor into the polymer. The curves of F/C before and after etching in

Fig. 5. XPS spectra of C_{1s} in PPHFP.

HFP: 2.5 sccm ; pressure: 10 Pa ; substrate: Al foil.

Upper: before etching ; lower: after 120 s of Ar ion etching.

Fig. 6. Effects of refrigeration of substrate on elemental composition of PPHFP.

HFP: 2.5 sccm ; pressure: 10 Pa ; substrate: Al foil.

* Calculated from peak areas of XPS spectra.

Fig. 6 (B) crossed each other in the RF power range of 10-20 W, although those in Fig. 6 (A) were on parallel lines, both of which peaked at 10 W. The distance of F/C curves in Fig. 6 (B) extended with increasing RF power and reached the same measure in Fig. 6 (A). The O/C at 230 °K was a little higher than that at 300 °K over the nearly whole range of RF power, 5-50 W.

These results suggest the following: PPHFP deposited on the substrate splitting off F atoms at ambient temperature and the monomer structure was preserved by consumption of the double bond at an appropriate RF power such as 10 W. However, when the reaction was carried out with a refrigerated substrate, HFP was polymerized on the surface and/or in the inside of the adhering layer with the efficient convection under appropriate supply of RF power such as 10-20 W. The increase in the RF power promoted the vaporization of HFP and made the mechanism of the polymerization close to that at ambient temperature. The O atoms remaining in the reactor were incorporated a little into the polymer, and their amount increased under the convection of the HFP layer because they were easy to be taken in by renewal of the surface of the HFP layer and were hard to be left out by mitigation of plasma impact. It appears that the convection of HFP was also a cause of the lower deposition rate at 50 W at 230 °K than that at 10 W at 300 °K although there were similarities between both the membrane properties of PPHFP prepared under these operative conditions.

3.2. Plasma Multi-phase Polymerization of Fluorocarbons

As described above, the refrigeration of the substrate was very effective to change the optimum RF power setting and the mechanism of polymerization. The availability of the method was expected when some of mixed monomers had a tendency toward ablation in

spite of being valuable. Plasma copolymerization of TFMS-OFCB-HFP was tried by use of this method. H₂O was added as a monomer since it effected suppression of reduction and elimination of sulfonic acid group included in TFMS. The reaction was allowed to proceed in the lower electrode temperature range of 250-270 °K. Spontaneous increase in temperature and quick refrigeration at approximately 30-min intervals alternated. In the range of temperature, TFMS (b.p. 435 °K) and H₂O are solids, and HFP is a gas. OFCB (m.p. 234 °K, b.p. 269 °K) is altered phases between a liquid and a gas. Therefore the following effects were expected: TFMS was concentrated on the substrate under suppression of its extremely high ablation function; HFP promoted polymerization efficiently consuming its double bond and formed firm molecular structure by the reaction in the gas phase; OFCB was polymerized without excessive crosslinking for high electrical conductivity and developed an affinity between TFMS and HFP.

The XPS spectra of C_{1s} and S_{2p} of the resultant copolymer are shown in Fig.7 compared to the case of the copolymer prepared in the range of 300-310 °K. The effects of the refrigeration of the substrate on the characteristics of the copolymer are tabulated in Table 1. The improvement of the efficiency of the deposition is obvious. The F/C was increased by the refrigeration as shown in Table 1, and the preservation of the C-F bonds and suppression of excessive crosslinking was observed clearly as higher intensities in the binding energy range of 289-293 eV in Fig.7. However there were some differences depending on the kind of substrate, the peak of -SO₃ at 168 eV appeared in Fig.7 (B) and (E) more distinctly than it does in Fig.7 (A) and (D). By means of refrigeration, the electrical conductivity showed a tendency to increase, which was related to lower crosslinking. These effects seemed to be caused by the

refrigeration of substrates under which the plasma polymerization proceeded in multiple phases.

4. Conclusion

The effects of the refrigeration of substrates described as above are summarized as follows:

Fig. 7. XPS spectra of C_{1s} and S_{2p} in plasma copolymer derived from TFMS-OFCB-HFP mixture. TFMS: 2.0 sccm, OFCB: 3.5 sccm, HFP: 2.0 sccm, H_2O : 5.0 sccm ; pressure: 20-23 Pa ; RF power: 2.0 W at 300-310 °K, 5.0 W at 250-270 °K ; substrate: DG, Al.
Spectra
Upper: before etching ; lower: after 120 s of Ar ion etching.
Left (A-E): C_{1s} ; right (A, B, D, E): S_{2p} .

Table 1. Effects of Refrigeration of Substrate on Characteristics of Plasma Copolymer of TFMS-OFCB-HFP Mixture^{a)}

Temperature (°K)	Deposition rate ^{b)} (Å/min)	Ratio of atom numbers ^{c)}			Electrical conductivity ^{d)} (S/cm)
		F/C	S/C	O/C	
300~310	7	0.53~0.83	0.01~0.14	0.12~0.48	2.4×10^{-9}
		↓	↓	↓	$\sim 6.1 \times 10^{-6}$
		0.18~0.66	0.01~0.21	0.09~0.61	
250~270	220	0.69~1.06	0.01~0.15	0.10~0.42	4.3×10^{-7}
		↓	↓	↓	$\sim 3.3 \times 10^{-5}$
		0.62~1.17	0.01~0.16	0.07~0.55	

^{a)}TFMS: 2.0 sccm, OFCB: 3.5 sccm, HFP: 2.0 sccm, H_2O : 5.0 sccm ; pressure: 20~23 Pa ; RF power: 2.0 W at 300~310 °K, 5.0 W at 250~270 °K.

^{b)}Substrate: glass.

^{c)}Calculated from peak areas of XPS spectra (C_{1s} , F_{1s} , S_{2p} , O_{1s}).
Before Ar ion etching → after 120 s of Ar ion etching.
Substrate: Al foil, Celgard 2500, Duragard 3401.

^{d)}Measured in 0.5 mol/L H_2SO_4 aq.

(1) The refrigeration of the lower electrode as a sample stage affected the phase of the monomer in a vacuum just as in normal atmospheric pressure. (2) The plasma polymerization under the refrigeration needed more RF power than that at ambient temperature. (3) The refrigeration of the substrates changed the mechanism of polymerization, contributing to the reaction not only in a gas phase but also in liquid or/and solid phases. (4) The refrigeration was effective to improve the efficiency of the polymerization under coexistence of the monomer tending toward plasma ablation. (5) Utilization of the difference in phases between the coexisting monomers, which was brought about by the refrigeration, enabled the control of the molecular structure of the functional polymer.

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References

1. Japan Society for the Promotion of Science, Committee 153 (Plasma Materials Science), Ed., *Handbook of Plasma Materials Science*, Ohm-sha Co., Tokyo (1992) pp.576-579, pp.620-631.
2. K. Yasuda, Y. Uchimoto, Z. Ogumi, and Z. Takehara, *J. Electrochem. Soc.*, **141** (1994) 2350.
3. N. Inagaki, S. Tasaka, and T. Kurita, *Polym. Bull.*, **22** (1989) 15.
4. N. Inagaki, S. Tasaka, and Y. Horikawa, *J. Polym. Sci., Polym. Chem. Ed.*, **27** (1989) 3495.
5. S. Kurosawa, N. Kamo, T. Arimura, A. Sekiya, Y. Horikawa, T. Kurita, S. Tasaka, and N. Inagaki, *J. Jpn. Oil Chem. Soc.*, **43** (1994) 1007.