Applications of plasma polymerization

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Abstract - Plasma etching of polymeric material and plasma
polymerization of monomers were performed by using two types of reactors,
which are a tubular type and a gas flow type reactor. Phenomena of
deposition and ablation of organic materials in low temperature plasma
are discussed in relation to the practical processes.

INTRODUCTION

Plasma chemical processes of organic material in low temperature plasma are given
attention in various fields of technical development. The principal processes are organic
thin film coating, surface modification and etching of polymeric substrate. The processes
are performed under irradiation of electrons, ions, protons and activated neutral
particles in a wide range of energy level. Therefore, the phenomena in the processes are
usually complicated and the process is difficult to be regulated. However, several kinds
of applications were attained because of technical developments of evacuation systems,
discharge power sources, diagnostics and surface analysis.

In this study, several experiments on plasma etching of polymeric material and plasma
polymerization were performed by using two types of reactors, which were a tubular type
and a gas flow type. The interaction between plasma and polymeric materials in low
temperature plasma will be discussed. Recent results of application will be also
introduced.

GENERAL FEATURES OF PLASMA CHEMICAL PROCESSES FOR ORGANIC MATERIALS

Effect of Energetic Particles Irradiation On Vinyl Polymers
It is well known that the plasma chemical process is affected by chemical properties of
polymeric materials under the plasma irradiation. Lawton et al.(ref. 1 and 2) classified
conventional vinyl polymers into two groups as shown in Table 1: those that become
degraded under high energy irradiation and those that become cross-linked. According to
Miller et al., there is a simple correlation of radiation effect and chemical structure
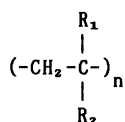of vinyl polymers which have a following generalized structure(ref. 2).

$$(-CH_2-C-)_n \quad \begin{matrix} R_1 \\ | \\ \\ | \\ R_2 \end{matrix}$$

TABLE 1. Effect of ionizing irradiation on vinyl polymers
(after Miller et. al., ref. 2)

Crosslinking	Degrading
Polyethylene	
Polymethylene	
Polypropylene	
Polystyrene	Polyisobutylene
Polyacrylic acid	Poly-α-methylstyrene
Polymethyl acrylate	Polymethacrylic acid
Polyacrylamide	Polymethyl methacrylate
Polyvinyl alkyl ethers	Polymethacrylamide

Crosslinking occurs when the polymer containes at least one α hydrogen atom. On the other hand, degrading occurs when the R_1 is CH_3 irrespective of the structure of R_2. Polyethylene and polystyrene are classified into crosslinking polymers, but polymethyl-methacrylate is α degrading polymer. Recently, Tsuda et al. studied theoretically the chemical reaction in the excited state of these polymers(ref. 3). Therefore, it is expected that different procedures must be adopted on the processes of polymerization, plasma etching and surface modification for the two types of polymers.

Etching of Polymeric Materials under the Irradiation of Plasma and Ion-beam
Etching phenomena of polymeric materials in gas phase have been studied under the irradiation of plasma and ion-beam.

Oxygen plasma etching was reported by Hansen(ref. 4), Hozumi(ref. 5), Taylor(ref. 6), et al. The weight loss of polymer was proportional to the discharge duration and the weight loss rate depended on the moleculer structure. Taylor et al. reported the relative etch rate of 40 polymer samples at a pressure of 73 Pa and a power of 100 Watts(ref. 6). The etch rate for polymer degraded by high energy radiation was proportional to the Gs value, the efficiency of chain scission per 100 eV of absorbed high energy radiation as shown in Table 2. The etch rates were also measured for polymer crosslinked by high energy radiation. Some polymers showed larger relative etch rates than those of polymers listed in Table 2. It was also shown that the strong backbone bonds, aromatic and polar functional groups and metallic atoms decreased the removal rates, but chlorine present in the polymer catalyzed removal.

TABLE 2. Relative rate K_{rel} of oxygen plasma removal and Gs values for selected
polymers degraded by high energy radiation(after Taylor et al., ref. 6)

Polymer	K_{rel}	Gs
Poly(α -methylstyrene)	1.11	0.3
Poly(phenyl methacrylate)	1.33	---
Poly(vinyl methyl ketone)	1.48	---
Poly(methyl methacrylate)	2.37	1.2
Poly(methyl methacrylate-co- methacrylonitrile)94.6 mole%	2.70	2.0
Poly(isobutylene)	3.56	4.0
Poly(butene-1 sulfone)	7.11	8.0
Poly(styrene)	1.00	

(The removal rate of polystyrene was 270 Å/min.)

Plasma etching by using other gases was also studied. Yasuda et al. measured weight loss rates of polymers under helium plasma at a pressure of 13.3 Pa and a discharge power of 30 Watts in a gas flow type reactor as shown in Table 3(ref. 7). Polymethacrylic acid showed relatively large weight loss rate even if it belongs to crosslinking polymer.

TABLE 3. Helium plasma etch rate of polymers
(after Yasuda et al., ref. 7)

Polymer	Weight loss rate ($mgcm^{-2}min^{-1}$)$\times 10^3$
Polyoxymethylene	17.0
Polyacrylic acid	16.2
Polymethacrylic acid	15.4
Polyvinylpyrrolidone	11.9
Polyvinyl alcohol	9.4
Polyethylene terephthalate	1.7
Polyethylene	1.2
Nylon 6	1.1
Polypropylene	0.8

Helium plasma: 13.3 Pa at 30 Watts.

Gokan et al. also reported that etch rates under argon and oxygen ion bombardment at energies of 300 and 500 eV are inversely proportional to the effective carbon contents in the polymer(ref. 8). However, it was observed that etching mechanism in oxygn plasma is quite different from that under ion bombardment. For the argon ion at the energy of 500 eV, the etch rate of certain polymers decreased after etching for a few minutes as shown in Fig. 1. On the contrary, no change in etch rate was observed during etching for all materials examined under the condition of 300 eV acceleration energy and about 0.3 mA/cm² current density. Ullevig and Evans reported also the decrease of etch rate of polymethyl methacrylate and polystyrene during the argon ion irradiation at an acceraration energy of 1 Kev(ref. 9).
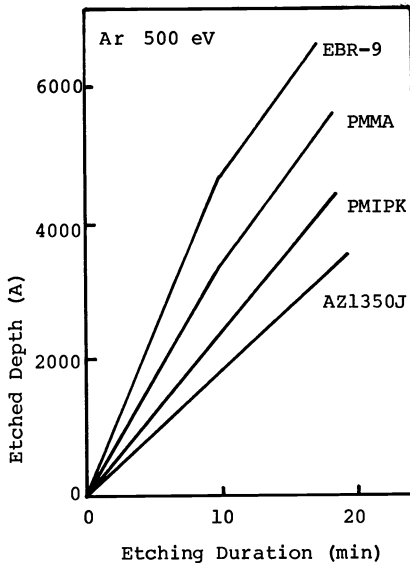

Fig. 1. Argon ion-beam Etched depth of typical polymers vs etching duration measured under 2.7×10^{-2} Pa argon pressure and 500 eV acceleration energy.

Usually, plasma etch rates of degrading polymers are relatively large compared to those of crosslinking polymers. However the absolute etch rate will be affected by molecular structure, constitutive atom ratio in the polymer and energy level of activated particles in the process. The etch rate usually increases with increasing oxygen ratio in the polymer.

Plasma Polymerization
Bradley et al. reported that plasma polymerization could be performed for any kind of monomer and the growth rate varied depending on the monomer structure even if polymerized films showed similar characteristics(ref. 10).

Effect of monomer structure on the plasma polymerization was studied by Yasuda et al. using pulsed radio frequency discharge(0.1 msec on and 0.9 msec off at a frequency of 13.56 MHz) at a lower pressure than 26.6 Pa(ref. 11). As shown in Table 4, pressure parameter δ and deposition rate of various monomers were measured in continuous and pulsed radio frequency discharge. The effects of pulsed discharge on the polymerization will be speculated from the co-relation between the change of pressure parameter δ and deposition rate. The author reported that the effect of the pulse was different from one group of organic compounds to another depending on whether or not they contain an olefinic double bond and/or a triple bond. The main difference seemed to be the addition polymerization which can occur exclusively during the off-period of pulsed discharge. Properties of polymers formed in continuous and pulsed discharge from some organic compounds were found to be significantly different, and the differences were postulated from the changes of polymerization mechanisms in pulsed discharge.

Buzzard et al. reported that linear chain polymer of tetrafluoroethylene could be formed on substrate placed in Faraday cage, in which radical can diffuse through wire netting from the discharge region(ref. 12).

These recent experiments suggest possibility of molecular design of polymer through plasma chemical process by controlling the discharge.

TABLE 4. Pressure parameter δ and growth rate of monomers in continuous and
pulsed radio frequency Discharges(after Yasuda et al., ref. 11)

Monomer	δ			Deposition rate $\times 10^{5} g/cm^{2}min$		
	Cont.	Pulsed	Change	Cont.	Pulsed	Change
Acetylene	0.10	0.30	+0.2(+200%)	31	21	-7(-23%)
Benzene	0.13	0.33	+0.2(+150%)	110	101	-9(-8%)
Hexafluoro benzene	0.10	0.15	+0.05(+50%)	190	149	-41(-22%)
Styrene	0.15	0.28	+0.13(+87%)	173	145	-28(-16%)
Ethylene	0.63	0.75	+0.12(+19%)	42	43	+1(+2%)
Tetrafluoroethylene	0.65	0.58	-0.07(-11%)	18	37	+19(+110%)
Cyclohexane	1.03	1.25	+0.22(+21%)	92	9	-83(-90%)
Ethylene oxide	1.45	1.38	-0.07(-5%)	15	14	-1(-7%)
Acrylic acid	2.00	1.43	-0.57(-29%)	28	61	+33(+120%)
Propionic acid	2.30	1.88	-0.42(-18%)	7	15	+8(+110%)
Vinyl acetate	2.25	2.13	-0.12(-5%)	31	16	-15(-48%)
Methyl acrylate	2.25	1.93	-0.32(-14%)	32	33	+1(+3%)
Hexamethyldisilane	1.50	1.20	-0.30(-20%)	251	65	-186(-74%)
Tetramethyldisiloxane	1.15	1.05	-0.10(-9%)	191	102	-89(-47%)
Hexamethyldisiloxane	1.50	1.15	-0.35(-23%)	233	43	-190(-82%)
Divinyltetramethyldisiloxane	0.73	0.75	+0.02(+3%)	641	277	-364(-57%)

$\delta = P_g/P_m$, where P_g is the pressure of a steady-state flow in glow discharge

P_m is the pressure of monomer before the discharge.

Changes are based on values of continuous discharge.

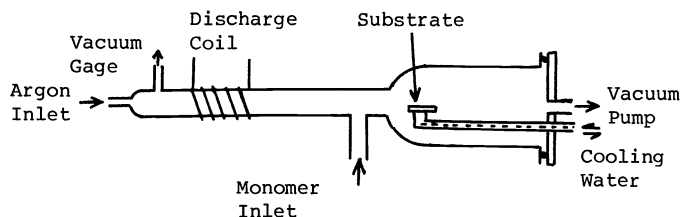## Application of Plasma Polymerization
Plasma chemical processes on organic materials are developing in various fields of
technology(ref. 13 to 21). Plasma chemical modification of polymer surface was applied
successfully for improvement of wettability, adhesion, and so on. Plasma polymerized films
were also developing as a dielectrics for thin film capacitor, a heat insulator with a low
melting point for huse(ref. 22), a layer for alignment of liquid crystal(ref. 23), an
insulator for pH sensor(ref. 24), an optical memory material(ref. 25), and so on.

EXPERIMENTAL

The experiments were performed by using two types of reactors as shown in Fig.2(a) and (b).
They are a tubular type reactor which is discharged by parallel plate electrodes and a gas
flow type which is discharged by an induction coil. The both reactors were operated at a
discharge frequency of 13.56 MHz.
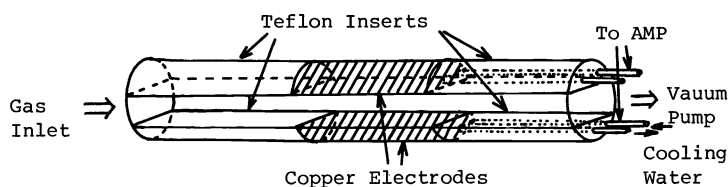
(a) Tubular Type Reactor

(b) Gas Flow Type Reactor

Fig. 2. Reactors for Plasma Etching and Plasma Polymerization.

RESULTS AND DISCUSSIONS

Plasma Etching of Polymeric Materials(ref. 26)
Plasma etching phenomena of polymeric materials were studied by using two types of
reactors with etching gases of oxygen(O_2), argon(Ar), nitrogen(N_2) and hydrogen(H_2).
Polymeric material was a cast sheet made of allyl-diglicol-carbonate(CR-39). The etch
rates were measured as shown in Table 5 and the plasma etched surfaces were also observed
by SEM.

TABLE 5. Plasma etch rate of CR-39

Gas Flow Type Reactor					Tubuler Type Reactor			
Gas	Flow Rate cc/min	Pressure Pa	Power Watts	Etch Rate $\mu g/cm^2 min$	Flow Rate cc/min	Pressure Pa	Power Watts	Etch Rate $\mu g/cm^2 min$
O_2	2.77	20	15	7.5	2.6	17	5	4.57
	16.95	47	15	23	2.6	17	10	9.19
	61.8	93	25	10.8	17	47	10	9.77
					53	86	10	10.48
Ar	2.55	20	25	4.93	3.06	20	5	2.6
	16.85	47	15	6.41	3.06	20	10	4.4
	16.9	47	25	7.08	17	56	10	5.88
	60	89	20	3.65	53	90	10	4.28
N_2	2.55	16	15	2.87	2.55	17	5	3.35
	2.55	16	25	2.63	2.55	17	15	6.82
	17	43	25	3.42	17	43	15	4.41
	53	80	25	2.02	53	80	15	3.01
H_2	2.55	12	25	1.22	2.55	12	5	2.57
	17	29	25	1.36	2.55	12	13	5.03
	17	31	12	0.81	17	28	15	4.07
	53	57	25	1.25	53	53	13	3.45

In case of the gas flow type reactor, the etch rate varied widely depending on the etching
gas. The etch rate by O_2 plasma was the largest among the used gases. However, in case of
the tubular type reactor, the variation of etch rates among the etching gases was not so
large compared with that in the gas flow type reactor. The transparent CR-39 substrate was
fogged by the Ar plasma treatment at the high pressure of about 120 Pa in the gas flow
type reactor. SEM pattern of the surface showed numerous pock marks as shown in Fig. 3(a).
But, the etched surface by other gas plasma was relatively smooth. As shown in Fig. 3(b),
the etched surface by oxygen is smooth in spite of the largest etch rate. Fogged surface
was not observed for the sample treated in the tubular type reactor at the experimental
condition.
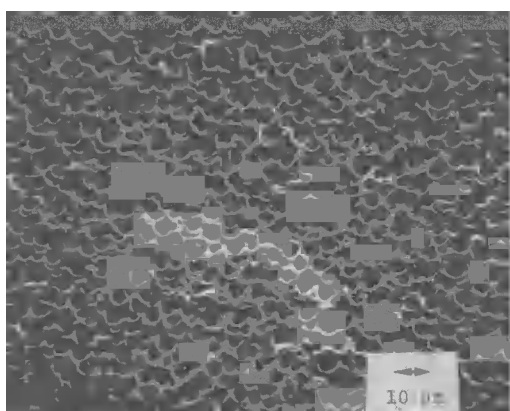
(a) Argon Plasma Etching
    Flow Rate: 53 cc/min,
    Pressure: 120 Pa,
    Power: 30 watts,
    Discharge Duration: 180 min.
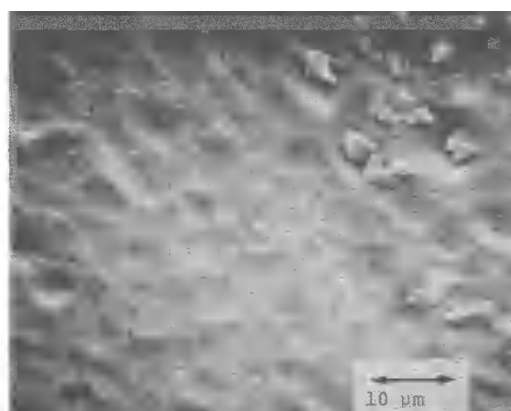
(b) Oxygen Plasama Etching
    Flow Rate: 53 cc/min,
    Pressure: 80 Pa,
    Power: 30 watts,
    Discharge Duration: 60 min.

Fig. 3. SEM patterns of plasma treated surfaces of CR-39

In the moderate glow discharge condition, it is supposed that ionized and neutral activated particles in the plasma affect on the etching phenomena differently in the two types of reactors. In the tubular type reactor, the etch rates did not distribute widely and it is thought that bombardment by ionized particles becomes significant. Whereas, it is supposed that sputtering of polymeric substrate by ionized particles is predominant mechanism of etching. Possibility of in-homogeneous sputtering by ionized particle bombardment will be rejected because ion bombardment at 300 eV formed smooth etched surface and the energy of ionized particles will not exceed 300 eV in the plasma(ref. 8).

However, the bombardment by ionized particles becomes to decrease in the gas flow type reactor, because there is no electrical field perpendicular to the substrate. Therefore, the plasma etching in the gas flow type reactor will be performed by chemical etching of ac;tivated neutral particles. The wide distribution of etching rates and pock marks formation will be referred to the chemical reactivity of etching gas plasma.

Plasma Polymerization of Crosslinking Polymer(ref. 27)
In this experiment, Ar and H_2 were used as carrier gases and methane and ethane were used as reaction gases in two types of reactors. In case of a gas flow type reactor, the deposition rate was too small to detect the film weight at the lower pressure than 20 Pa. However, methane and ethane were polymerized on the silicon wefa placed on the lower electrode at the same pressure by using the tubular type reactor. The molecular structure was studied by Fourier Transform Infrared Spectroscopy(FT-IR). FT-IR spectra of the films showed that the absorption peaks belonging to C-H and C=C bonds were negligibly small as shown in Fig. 4. As shown in Table 6, the refractive index ranged between 1.8-2.6 which was larger than that of conventional polyethylene(about 1.5). The films were transparent at the optical wave length and hardness of the film was higher than that of the film formed at higher pressure than 50 Pa.
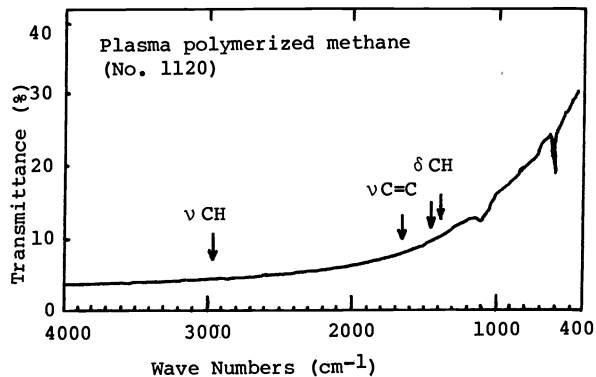

Fig. 4. FT-IR spectra of plasma polymerized methane(Sample No. 1120)

TABLE 6. Refractive index of plasma polymerized methane and ethane formed by tubular type reactor

No. of Sample	Carrier Gas (Flow Rate) SCCM	Pressure Pa	Monomer (F. R.)P.	Power W.(W/cm)	Discharge Duration hr	Thickness Å	Refractive Index
1113	Ar(3.32)	24	(0.34)0.19	25(0.25)	4	---------	----------
1114	Ar(3.32)	23	(0.33)0.20	45(0.45)	4	900, 1000	1.85
1120	Ar(3.32)	19	(0.33)0.17	45(0.90)	2.5	600	2.6
1122	Ar(3.32)	23	(0.27)0.19	40(0.80)	4	290	2.1-2.2
Ethane	-----------	--------	(20.5)0.20	15(1.11)	1	400	2.0

Carbon atom was detected by ESCA measurement. But at the same time, fluorine(F), aluminium (Al), silicon(Si), and oxygen(O) atoms were also contained in the film. The contamination was decreased markedly by covering the polyterafluoroethylene(Tefron) insert with polyethylene film and the deposition rate of the film was improved apparently. Therefore the contamination was referred to the dissociated F atom from the Tefron insert in the reactor, which etched off Al from Al foil covering the discharge electrodes and Si and O from the glass wall. It is thought that the dissociation of F atom from the tefron insert was enhanced at the low pressure, because the glow region of discharge is diffused into the whole reactor.

Detected aluminium and fluorine atom in the film were supposed to be contained in the form of trifluoroaluminium(AlF₃), because chemical shift of aluminium and fluorine in ESCA signal indicated existence of AlF_3 structure (ref. 27). Stepwise dissociation energy of AlF_3 is 6.77 eV, 4.60 eV and 6.90 eV respectively(ref. 28). Whereas, it is supposed that the ion bombardment was not so serious to dissociate AlF_3.

Low concentration of C-H and C=C structure in the film suggests that molecular structure of the film is quite different from usual plasma polymerized hydrocarbon which contains crosslinked polymer chains and unsaturated bonds. The reason for decreased concentration of C-H and C=C bonds in the film is not apparent from this experiment. Tsuda presented the result of theoretical calculation that activation energy of reaction of hydrogen atom with C=C structure is zero(ref. 29). Whereas it is not impossible for the hydrogen atom to act as a catalyzer on the film formation.

Plasma Polymerization of Degrading Polymer
In the gas flow type reactor, it was observed that the bubbles appeared in the plasma polymerized film and gr w up gradually when methyl-methacrylate(MMA) gas was introduced into the down stream of hexafluorosulphide(SF_6) and Ar mixture gas plasma. After two hours of discharge, the maximum diameter of the bubbles reached 8 mm as shown in Fig. 5(ref. 30). Typical plasma polymerization was performed at a gas pressure of 93 Pa, a discharge power of 30 watts, an argon flow rate of 40 cc/min, a SF_6 flow rate of 10.6 cc/min, a MMA flow rate of 5.3 cc/min and a room temperature. This is curious phenomena for the plasma polymerization.

In order to study the reaction mechanism, several carrier gases were used for the plasma polymerization of MMA. The deposition rates were measured as shown in Table 7(ref. 31). When the monomer gas feed was stopped, the weight loss of polymerized film was observed at the same discharge condition as shown in the same table.

NMR spectra were measured for the polymers dissolved into the deuterized benzene from the plasma polymerized films. By analyzing NMR spectra, radical and ionic mechanisms in the polymerization were distinguished(ref. 31). Radical mechanism was expected to be important in an inert gas plasma at a lower pressure than about 50 Pa. Ionic mechanism was observed in O_2 and SF_6 carrier gas, and also in inert gases at a higher pressure. From these experiments, it is summarized that usually radical reaction is observed in the plasma polymerization, but ionic reaction becomes predominant when the ions surrounded by monomers with dipole was adsorbed on the substrate.
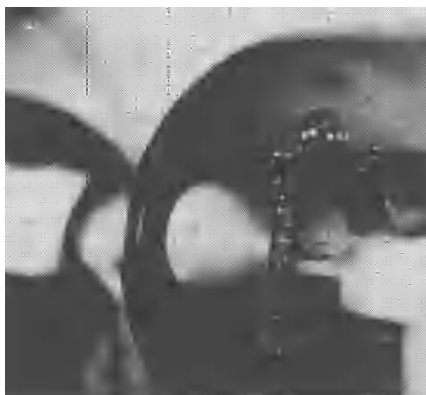

Fig. 5. Bubbles formed by plasma polymerization using SF_6-Ar-MMA mixture glow discharge(same photograph appeared in ref. 30)

TABLE 7. Deposition rate of plasma polymerized MMA by gas flow type reactor(after Hori et al., ref. 31)

Carrier Gas	Flow rate cc/min	Pressure Pa	Power Watts	Deposition Rate $\mu g/cm^2 min$
O_2	50	67	10	2.6
	50	106	10	-3.4
Ar	50	67	10	1.0
Ar	50	67	10	-5.8
(O_2)	(50)	(80)	(15)	(-6.8)
N_2	50	67	10	0.5
	50	67	10	-0.8
H_2	115	67	10	0.7
	115	67	10	-1.8

Plasma Polymerization on Plastic(ref. 32)
As a protective and transparent film coating on the plastics like as CR-39, plasma polymerization of organo silicon in O_2 plasma was proposed to be useful. In case of a tubular type reactor, tetrametylsilane(TMS) and O_2 mixture gas plasma could not deposit the film on the substrate and only weight loss of substrate was observed at an usual plasma polymerization condition. However, the polymerized film was observed on glass and NaCl crystal substrate in the same discharge. This fact means that ablation of CR-39 under the irradiation of plasma was more significant compared to deposition of polymerized film onto the substrate. When plasma polymerized styrene was under-coated on CR-39, plasma polymerized TMS could be deposited successfully.

When the gas flow type reactor was used, plasma polymerization of TMS in O_2 plasma was performed on the CR-39 substrate succesfully without under-coating. When dimethyl-dimethoxy-silane(DMDMOS, $Me_2Si(OMe)_2$) was used as a monomer, the plasma polymerized film showed the excellent properties as a protective coating on CR-39 for an optical application. Its properties are adhesion, hardness and transparency. Organo silicon is known to be useful as a binder between plastics and selamics. As shown in Fig. 6, plasma polymerized DMDMOS in O_2 plasma indicated absoption peaks around 2900 cm^{-1}, 1270-1255 cm^{-1}, 1100-1000 cm^{-1} and 820-900 cm^{-1} which are assigned to C-H stretch, Si-CH_3 bend, Si-O stretch and Si-H bend, respectively. Whereas these molecular structures sustain the good adhesion, hardness and transparent properties. Relative transmittances of the films are shown in Fig. 7.
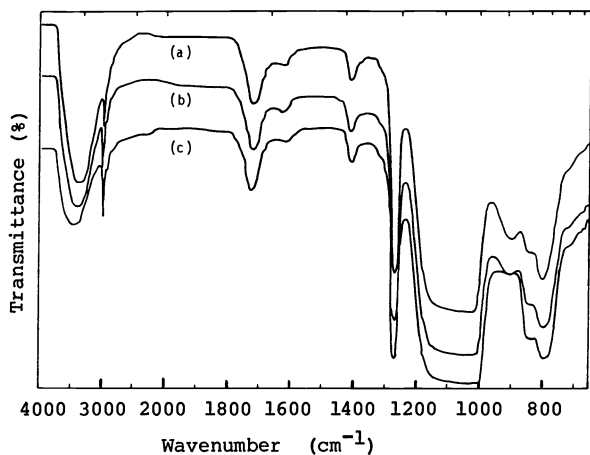

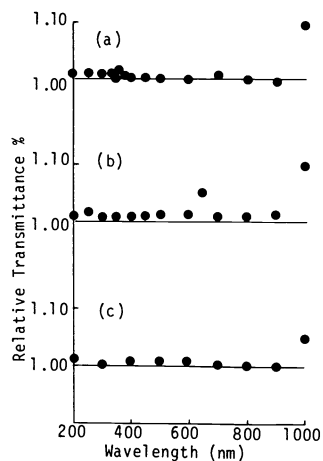Fig. 6. Infra-red spectra   Fig. 7. Relative transmittance

Samples of plasma polymerized DMDMOS-O films:
oxygen gas flow rate of 15 cc/min, DMDMOS flow rate of 2.1 cc/min,
pressure of 47 Pa and discharge duration of 30 min, discharge powers
(a) 30, (b) 35 and (c) 50 Watts.

PLASMA CHEMICAL PROCESSES IN VACUUM LITHOGRAPHY

A completely dry lithography has been proposed which involves plasma polymerization for resist coating and plasma development. It was named vacuum lithography because all processes are performed in vacuum. Plasma polymerized resist is an example of functional polymer.

There have been a significant improvement in the sensitivity of plasma polymerized dry developable electron beam resists so far we tried, as listed in Table 8. The development have been brought about first by employing gas flow type plasma reactor then by using co-polymerization with plasma etch resistive monomer and by adopting heavy atom sensitization.

TABLE 8. List of electron beam resists formed by plasma polymerization and
developed by plasma etching

Type of Reactor	Monomers	Polymerization Plasma	Developing Plasma	Sensitivity $\mu C/cm^2$	Reference
Parallel Plate	MMA	MMA	CCl_4	$>10^4$	33
Flow	MMA	Ar	$Ar+O_2$	10^3	34
Flow	MMA+Styrene	Ar	$Ar+O_2$	10^2	35
Flow	MMA+TMT	Ar	$Ar+O_2$	20	34
Flow	6FBMA+Styrene	Ar	H_2	10^2	35
Flow	6FBMA+Styrene+TMT	Ar	H_2	5	35

By using a vacuum lithography, a photomask of sputtered chromium film was fabricated successfully on glass substrate. Fabricated pattern was 4 μm lines and spaces as shown in Fig. 8.
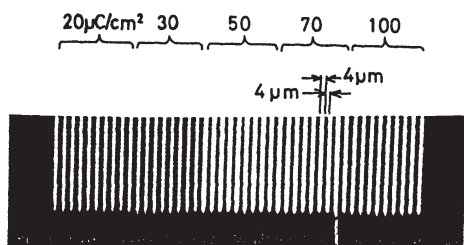
Fig. 8. A photomask fabricated on chromium
       by vacuum lithography
       (after Tamano et.al., ref. 36)

Fig. 9. An X-ray imaged triangle pattern
       on plasma polymerized resist, which
       was developed by hydrogen plasma.
       (after Hori et al., ref. 37)

The quality of plasma polymerized resist was also evaluated in X-ray lithography processes. An X-ray(1.54 Å, Cu Target at 20 KV, 40 mA) was irradiated through a window of Au sheet (50 μm thickness) on the plasma polymerized MMA. The latent pattern formed at 4.1 J/cm² was successfully developed by H_2 plasma as shown in Fig. 9.

An X-ray mask was proposed to be formed by the vacuum lithography. Au containing plasma polymerized styrene(Au+PPS) is expected to be used as an X-ray absorbing material. The mask pattern was fabricated on Au+PPS formed on Si wefa as shown in Fig. 10. The procedures of mask fabrication were as following; resist of plasma polymerized 6FBMA was deposited on Au+PPS, 4 μm lines and spaces were delineated by an electron beam of 4 X 4 μm² spot, the delineated patterns on the resist were developed by oxygen plasma, Au+PPS was etched through the mask of resist by carbon dioxide plasma.
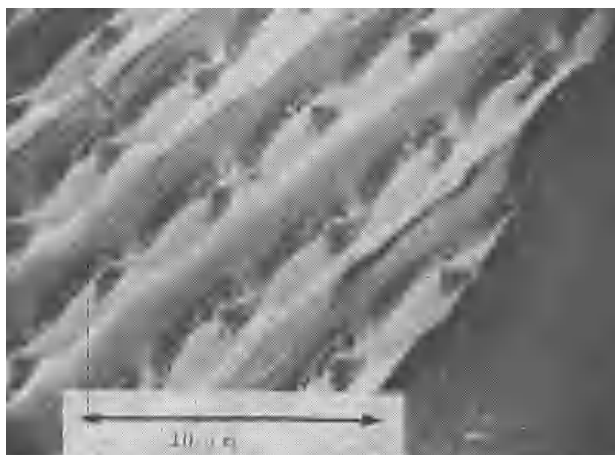

Fig. 10. An X-ray mask fabricated by electron beam vacuum lithography.
        X-ray absorber; mixture of evaporated gold and plasma polymerized
        styrene, resist; plasma polymerized hexa-fluorobutyl-methacrylate
        electron beam; 4 μm X 4 μm spot(after Yoneda et.al., ref. 38).

CONCLUSIONS

Plasma chemical processes reviewed were related to interaction between plasma and organic materials. Phenomena of deposition and ablation in the plasma were introduced by using actual experimental results. Recent developments of plasma chemical processes in vacuum lithography were also presented.

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