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유기실리콘화합물의 플라즈마 중합에 관한 연구 : 1. 플라즈마 중합막의 화학구조

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Plasma Polymerization of Organosilicon Compounds : 1. Chemical Structure of Plasma Polymer

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요 약 : 테트라메칠실란(TMS), 헥사메칠디실라잔(HMDSIZ), 헥사메칠디실록산(HMDSIO)의 플라즈마 중합에 의한 유기실리콘 박막의 형성에 있어 중합의 에너지 조건 (W/Fm)이 생성박막의 화학구조에 미치는 영향을 FTIR과 XPS 분석에 의해 상세히 검토하였다. 생성박막의 화학구조적 특성은 10^7 J/kg-10^9 J/kg 범위의 W/Fm값 조절에 의해 체계적이고 대폭적인 변화를 보였으며 이러한 화학구조의 변화는 플라즈마 중합의 활성화 성장기구에 의해 설명되었다.

Abstract : Thin organosilicon films were obtained by the plasma polymerization of tetramethylsilane (TMS), hexamethyldisilazane(HMDSIZ), and hexamethyldisiloxane(HMDSIO). The effect of input energy level (W/Fm) on the chemical structure of the plasma polymer was investigated by using FTIR and XPS measurements. The structural characteristics of the plasma polymer were significantly altered by the value of W/Fm (over the range of 10^7 J/Kg to 10^9 J/Kg). The unique and notable influence of W/Fm on the chemical structure was interpreted in relation to the *activation growth* mechanism of the plasma polymerization.

INTRODUCTION

Recently, interest in the thin organic films prepared by plasma polymerization process is increasing rapidly since these materials display excellent physical and chemical properties.[1,2] Great research efforts have been focused on the technological applications of these films, for example, electronic[3~8] or optical[9~12] devices, separation membranes,[13,14] protective coatings,[15] and biomedical materials.[16] However, our understanding of the plasma polymerization process itself is limited due to the highly complex nature of the plasma process.[1a,2]

In contrast to the conventional *polymerization reaction*, the chemical structure of plasma polymer is significantly altered by the operational parameters chosen for the *plasma polymerization reaction.*[1b] Thus, it is expected that the careful analysis of the structural change as the function of operational parameters may allow us to gain some insights into the mechanism of the plasma polymerization. Many workers already reported the pronounced effects of operational parameters including the discharge power (W), mass flow rate (Fm), system pressure, substrate temperature, etc..[1b,c,d] However, only qualitative and limited informations for the plasma polymerization process could be obtained from these studies since it was difficult to account for the microscopic environment of molecules in a discharge state with those parameters. Recently, Yasuda and Hirotsu[17] have shown that the input energy level of glow discharge, that means the energy input per individual molecule, should play an important role in the control of chemical structure. As a quantitative measure of input energy level, they proposed a composite parameter W/Fm. Since the discharge power (W) is the rate of energy supply and the mass flow rate (Fm) is the rate of monomer supply to the plasma reactor, it is apparent that W/Fm is a proper measure of the average energy delivered to the unit mass of monomer in a discharge state. The importance of this parameter in controlling the structure, properties, and deposition rate of the plasma polymer is well demonstrated in the recent book of Yasuda.[1] In our previous work,[18a] we also noticed the uniqueness of this parameter in controlling the chemical structure, density, and deposition yield of HMDSIZ plasma polymer. Moreover, we could derive a new kinetic equation for the deposition rate of the plasma polymer based on the "*activation growth*"[19] ("*rapid step-growth*"[1b]) reaction which comprehensively explained the systematic changes of structure, density, and deposition yield in terms of W/Fm.

In the present series of works, we extended our previous work[18a] to several organosilicon monomers (TMS, HMDSIZ, HMDSIO) and also characterized the materials more thoroughly using additional techniques such as XPS analysis. We investigated the detailed effects of W/Fm on the chemical structure (Part I), physical properties (Part II),[18b] and deposition rate (Part III)[18c] with the aim of gaining better insights into the plasma polymerization process.

EXPERIMENTAL

Plasma Polymerization

The plasma reactor consists of a Pyrex bell-jar (ca. 8 liter volume) with a pair of stainless steel discharge electrodes as shown in Fig. 1. The upper electrode (6 cm diameter) fitted with monomer introducing holes at the bottom side was connected to the 13.56 MHz RF generator via an impedance matching circuit and the lower electrode (10 cm diameter) was grounded. Prior to the electric discharge, liquid monomer (TMS, HMDSIZ, or HMDSIO) was charged into the reservoir, and was degassed by the freeze-thaw method. The system pressure before discharge(P_o) was monitored by a Pirani vacuum gauge without specific calibration of gauge reading for each vapor. The whole system was initially evacuated down to 10^{-3} torr using a mechanical vacuum pump (Edwards, model E2M-18). Then, the reactor was exposed to the full-glow argon plasma (50 watt, 50 millitorr) for five minutes to eliminate moisture adsorbed on the subst-

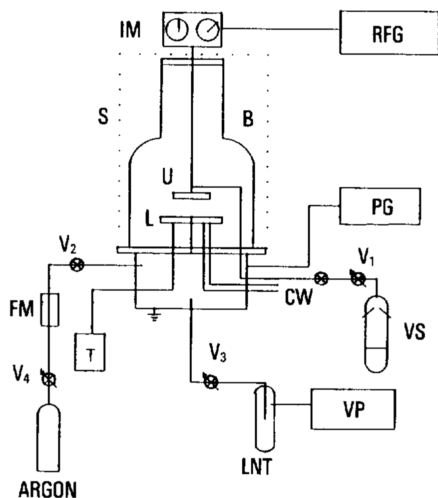


Fig. 1. Schematic diagram of plasma polymerization reactor : (RFG) RF generator ; (IM) impedance matching circuit ; (B) bell-jar ; (S) RF shield ; (PG) pressure gauge ; (U) upper electrode, powered ; (L) lower electrode, grounded ; (VS) monomer reservoir ; (V_1) micrometering valve ; (V_3) throttle valve ; (CW) cooling water ; (FM) flow meter ; (T) thermocouple and heater ; (LNT) liquid nitrogen trap ; (VP) vacuum pump.

rate surfaces and the reactor wall. After re-evacuation of the system down to 10^{-3} torr, monomer vapor was introduced into the reactor through the bottom holes of the upper electrode. The main reason of this flow configuration was to make all the monomer flow through the glow region between a pair of electrodes since the plasma volume and the intensity of glow were highly dependent on the operational parameters. The flow rate of monomer vapor was adjusted by a micrometering valve (Nupro SS-4BMG) while the down-stream throttle valve was kept fully open throughout the experiments. The mass flow rate of monomer (Fm) was determined by cutting off the vacuum pump and monitoring the initial increase of system pressure with time.[1d] In practice, Fm was varied over 5-150 mg/min range which resulted in the observed changes of P_0 over 40-200 millitorr. Following the stabilization of flow rate, the glow discharge was initiated and continued over 20 minutes at a fixed discharge power (W) level. Since W was chosen from the range of 10-100 watt, the range of W/Fm value was 10^7 to 10^9 J/Kg. During the glow discharge, the substrate on the lower electrode was constantly cooled by tap water.

FTIR Spectra

FTIR spectra of plasma polymers deposited on aluminum foil were taken by the external reflection method (single reflection, 64 scans, 4 cm^{-1} resolution) using the Mattson Alpha-Centauri FTIR spectrophotometer. Alternatively, FTIR spectra of plasma polymers deposited on KBr plate were taken using the Analect FX-6160 FTIR spectrophotometer at 16 scans, 4 cm^{-1} resolution. Also the spectra of monomers (TMS, HMDSIZ, HMDSIO) and polydimethylsiloxane (Polyscience, Cat. #2317) were taken at 8 scans, 4 cm^{-1} resolution using the Analect FTIR spectrophotometer.

XPS Spectra

Plasma polymer films were deposited on aluminum foil and were stored in a desiccator (over phosphorous pentoxide) before obtaining the XPS spectra. XPS spectra were taken with a Physical Electronics PHI 558 electron-spectrometer employing MgK α exciting radiation (300 W, 12 kV). Binding energy of the individual photoionization peak was calibrated referencing to that of the major C_{1s} level at 285.0 eV. Atomic composition of the surface was calculated from the normalized area of each photoionization peak using the sensitivity factors.[20]

RESULTS

FTIR spectra of three organosilicon monomers are shown in Fig. 2, and those of corresponding plasma polymers deposited at the relatively low input energy level (W/Fm < 30 MJ/Kg) are shown in Fig. 3. The monomer spectra are well identified by the absorption bands of $Si-CH_3$ at 2956-2965, 2898-2909, 1254-1259, 842-867 cm^{-1}, and Si-C at 600-800 cm^{-1} for all the three monomers ; Si-N-Si at 934 cm^{-1}, and N-H at 3381 and

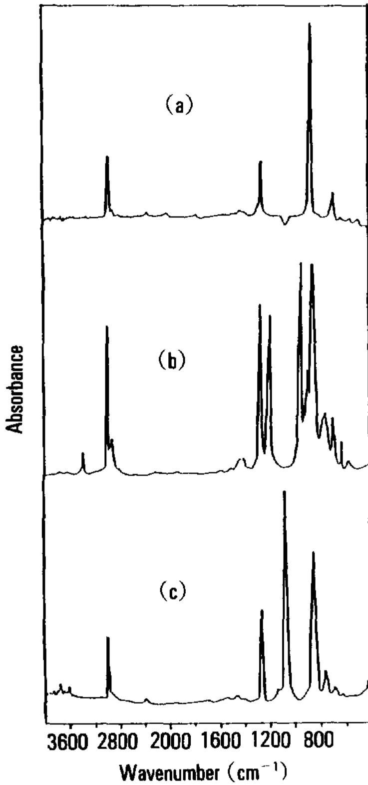


Fig. 2. FTIR spectra of organosilicon monomers. (a) TMS, (b) HMDSIZ, (c) HMDSIO.

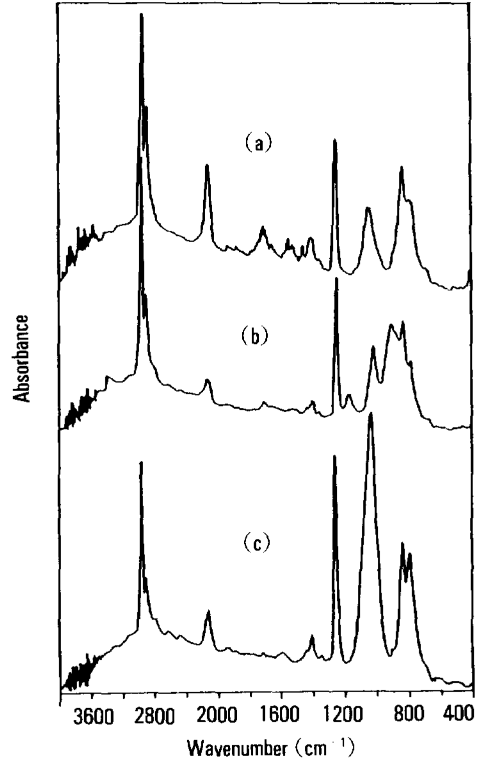


Fig. 3. FTIR spectra of organosilicon plasma polymers formed at the low input energy level (spectra taken by external reflection method) : (a) TMS plasma polymer at W=50 watt, Fm=99.2 mg/min, P_o=200 millitorr, W/Fm=30.2 MJ/Kg, (b) HMDSIZ plasma polymer at W=50 watt, Fm=146.2 mg/min, P_o=200 millitorr, W/Fm=20.5 MJ/Kg, (c) HMDSIO plasma polymer at W=50 watt, Fm=142.6 mg/min, P_o=200 millitorr, W/Fm=21.0 MJ/Kg.

1182 cm^{-1} for HMDSIZ ; Si-O-Si at 1073 cm^{-1} for HMDSIO, as summarized in Table 1 for each monomer. The polymer spectra shown in Fig. 3 are composed not only of the corresponding monomer bands but also of several new absorption bands which were absent in monomer spectra (marked as * in Table 2), namely, Si-CH_2-Si/Si-CH_2-CH_2-Si at 2928, 1430, 1350, 1030, 792 cm^{-1}, and Si-H at 2125cm^{-1}. Also, the absorption bands due to the probably oxidized structure are found in the spectra of plasma polymers, such as O-H at 3400cm^{-1}, C=O at 1705cm^{-1}, and Si-O-Si at around 1050cm^{-1}. Although the relative absorbances of all the component bands changed according to the operational parameters W or Fm, it was found that the observed spectral changes could be uniquely related to the value of W/Fm as demonstrated in our previous work with HMDSIZ.[18a] Thus, we could investigate the spectral changes only in terms of the input energy level W/Fm. Fig.'s 4-6 show the spectral changes of TMS, HMDSIZ, and HMDSIO plasma polymers with increasing W/Fm. Attention should be called to the fact that the spectra were taken using a transmission technique instead of using an external reflection technique since the relative intensity of each component peak in the reflection absorption spectra is significantly affected by the frequency and the thickness of thin

Table 1. IR Band Assignment of Organosilicon Monomers

Material	Peak Position (cm^{-1})	Band Assignment[21~23]
TMS	2963	ν_a(C-H) in CH_3
	2899	ν_s(C-H) in CH_3
	1254	$\delta_s(CH_3)$ in Si-CH_3
	867	$\rho(CH_3)$ in Si-CH_3
	695	ν(Si-C)
HMDSIZ	3381	ν(N-H)
	2956	ν_a(C-H) in CH_3
	2898	ν_s(C-H) in CH_3
	1400	$\delta_a(CH_3)$ in Si-CH_3
	1254	$\delta_s(CH_3)$ in Si-CH_3
	1182	δ(N-H)
	934	ν_a(Si-N-Si)
	851,842	$\rho(CH_3)$ in Si-$(CH_3)_3$
	755-618	ν(Si-C)
HMDSIO	2965	ν_a(C-H) in CH_3
	2909	ν_s(C-H) in CH_3
	1259	$\delta_s(CH_3)$ in Si-CH_3
	1073	ν_a(Si-O-Si)
	850	$\rho(CH_3)$ in Si-$(CH_3)_3$
	758,687	ν(Si-C)

ν : stretching, δ : bending, ρ : rocking,
a : asymmetric, s : symmetric.

film, thus making the quantitative interpretation of spectra greatly complicated.[24] The most prominent spectral change associated with the increase in W/Fm is the gradual reduction of absorption intensities due to Si-CH_3 (1254, and 2956 cm^{-1}) with the simultaneous increase of absorption intensities due to Si-CH_2-Si/Si-CH_2-CH_2-Si(2928, 1030cm^{-1}). Also, the stretching vibration bands in 1100-600 cm^{-1} region (such as Si-O, Si-C, Si-N, C-C) gradually broaden and increase their overall intensity with increasing W/Fm, which means the gradual transformation into the complex chemical structure with enhanced inorganic character.[25] Fig. 7 shows the absorbance ratio of CH_2 (2926 cm^{-1}) to CH_3 (2956 cm^{-1}), and Fig. 8 shows that of Si-H (2125 cm^{-1}) to Si-CH_3 (1256 cm^{-1}) as a function of W/Fm. From the figures, it is apparent that these

Table 2. IR Band Assignment of Plasma Polymers

Peak Position*[1] (cm^{-1})	Band Assignment[21~23]	Plasma Polymer*[2]
3400*	ν (O-H)	S,Z,X
3370*	ν (N-H)	Z
2956	ν_a(C-H) in CH_3	S,Z,X
2928*	ν_a(C-H) in CH_2	S,Z,X
2902	ν_s(C-H) in CH_3	S,Z,X
2856*	ν_s(C-H) in CH_2	S,Z,X
2125*	ν (Si-H)	S,Z,X
1705*	ν (C=O)	S,Z,X
1430*	$\delta_a(CH_2)$ in Si-CH_2-CH_2-Si	S,Z,X
1400	$\delta_a(CH_3)$	S,Z,X
1350*	$\delta_a(CH_2)$ in Si-CH_2-Si	S,Z,X
1254	$\delta_s(CH_3)$ in Si-CH_3	S,Z,X
1180	δ (N-H)	Z
1100-1000*	ν_a(Si-O-Si), ν_a(Si-O-C)	S,Z,X
1030*	ω (CH_2) in Si-$(CH_2)_n$-Si	S,Z,X
920-900	ν_a(Si-N-Si)	Z
840	ρ (CH_3) in Si-$(CH_3)_n$, n=2,3	S,Z,X
792*	ρ (CH_3) in Si-$(CH_3)_n$, n=1,2	S,Z,X
900-500	ν (Si-C)	S,Z,X

ν : stretching, δ : bending, ω : wagging, ρ : rocking, a : asymmetric, s : symmetric, * : peak absent in the monomer spectra, *[1] : The seemingly sharp absorption peak centered at around 600-700 cm^{-1} is not the real absorption peak of plasma polymer but the absorption due to the atmospheric CO_2 which was difficult to eliminate since the plasma polymer sample was extremely thin (0.1-0.3 μm).
*[2] : (S) TMS, (Z) HMDSIZ, (X) HMDSIO

ratios steadily increase with increasing W/Fm.

Survey-scan XPS spectra of three organosilicon plasma polymers are shown in Fig. 9. The signals from silicon (Si_{2p} at 102 eV, Si_{2s} at 153 eV), carbon (C_{1s} at 285 eV), and oxygen (O_{1s} at 535 eV, O Auger at 743 eV) atoms were detected in all plasma polymers of TMS, HMDSIZ, and HMDSIO. However, the signals from nitrogen atom (N_{1s} at 400 eV, N Auger at 875 eV) were detected only in the plasma polymer of HMDSIZ which has the N element in the monomer structure. High resolution spectra of Si_{2p}, C_{1s}, O_{1s}, and N_{1s} core electrons

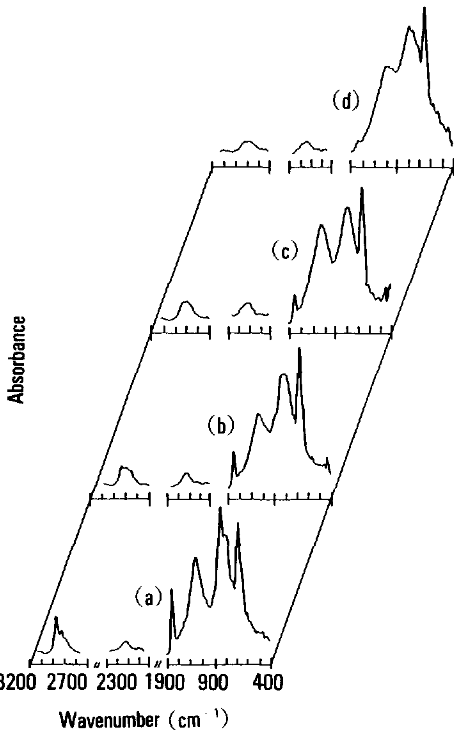


Fig. 4. FTIR spectra of TMS plasma polymer as a function of W/Fm (MJ/Kg) : (a) 31.2, (b) 93.5, (c) 155.8, (d) 311.5.

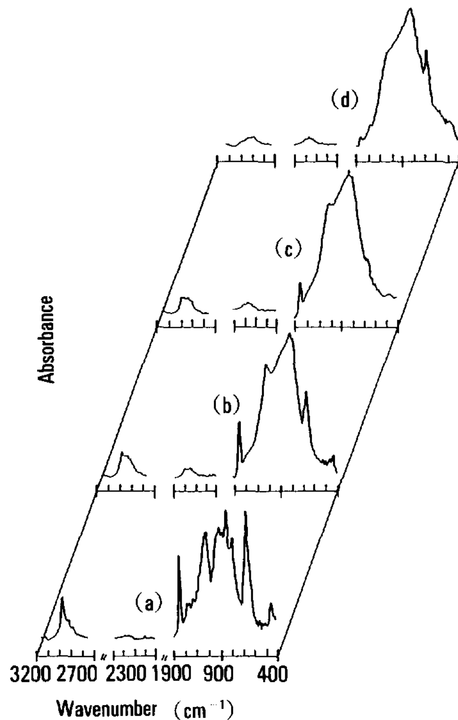


Fig. 5. FTIR spectra of HMDSIZ plasma polymer as a function of W/Fm (MJ/Kg) : (a) 25.2, (b) 75.5, (c) 125.8, (d) 251.6.

were also recorded as a function of W/Fm. Generally, it was difficult to monitor the effect of W/Fm on the changes of chemical structure in detail by these XPS spectra due to the limited binding energy shift corresponding to the changes of chemical environment. However, these spectra were powerful in monitoring the changes of surface elemental compositions of plasma polymers. Fig.'s 10-12 show the variation of C/Si, O/Si, and N/Si ratio as a function of W/Fm for TMS, HMDSIZ, and HMDSIO plasma polymer, respectively. It is seen that the C/Si ratio initially increases with W/Fm, then decreases after passing through the maxima at around 100-150 MJ/Kg. The O/Si ratio of TMS and HMDSIZ plasma polymer increases steadily with W/Fm, on the other hand, that of HMDSIO plasma polymer shows a maximum at around 100-150 MJ/Kg. The N/Si ratio of HMDSIZ plasma polymer is not much affected by W/Fm.

DISCUSSION

Plasma polymerization of organosilicon monomers has been widely investigated due to the excellent thermal,[26] electrical,[27] optical,[11] biomedical,[16] and membrane[28] properties of the plasma polymerized film. Moreover, these monomers are of great interest due to the high deposition rates and the systematic changes in the chemical structure of the plasma polymer by the operational parameters of plasma reaction.[1b,18]

Although the plasma polymerization is an extremely complex process, it is generally agreed that the monomer molecules introduced into the plasma are activated into reactive fragments, which then recombine to form new chemical bonds.[1b,19]

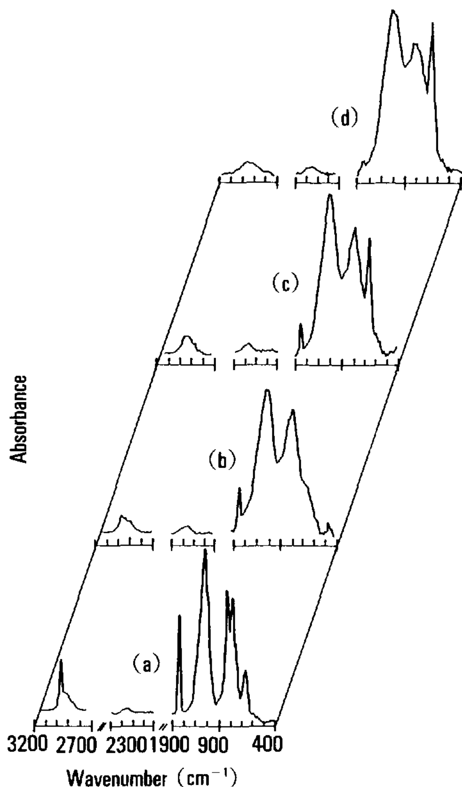


Fig. 6. FTIR spectra of HMDSIO plasma polymer as a function of W/Fm (MJ/Kg) : (a) 22.5, (b) 67.5, (c) 112.5, (d) 224.9.

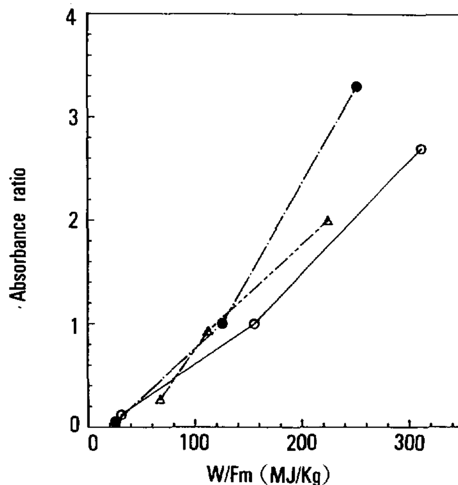


Fig. 7. IR absorbance ratio of methylene (2928 cm^{-1}) to methyl (2956 cm^{-1}) group as a function of W/Fm in the plasma polymers of (○) TMS, (●) HMDSIZ, and (△) HMDSIO.

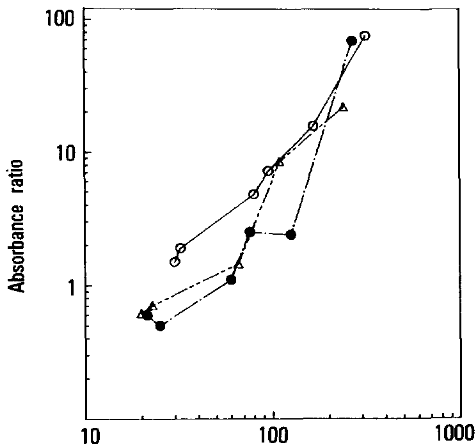
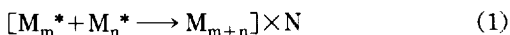


Fig. 8. IR absorbance ratio of Si-H (2125 cm^{-1}) to Si-CH_3 (1256 cm^{-1}) group as a function of W/Fm in the plasma polymers of (○) TMS, (●) HMDSIZ, and (△) HMDSIO.

The repetition of these activation and mutual recombination reaction of monomer molecules in a plasma possibly leads to the deposition of the plasma polymer whose chemical structure consists of a randomly cross-linked covalent network. This reaction scheme is called either a "rapid step-growth polymerization (RSGP) mechanism" by Yasuda[1b] or an "activation growth mechanism" by Vinogradov.[19] (We prefer the term "activation growth" in this work).



$$[M_m^* + M_n^* \longrightarrow M_{m+n}] \times N \quad (1)$$

The asterisk(*) in eq 1 means an activated species and ×N means the number of repetition of similar reaction. Recently, evidences supporting this model were reported through the diagnosis of polymerizing plasma, the characterization of the chemical structure and physical properties of the plasma polymer, and the investigation of the deposition kinetics.[1b,c,d,18a] Most importantly, the experimentally observed systematic variation of chemical

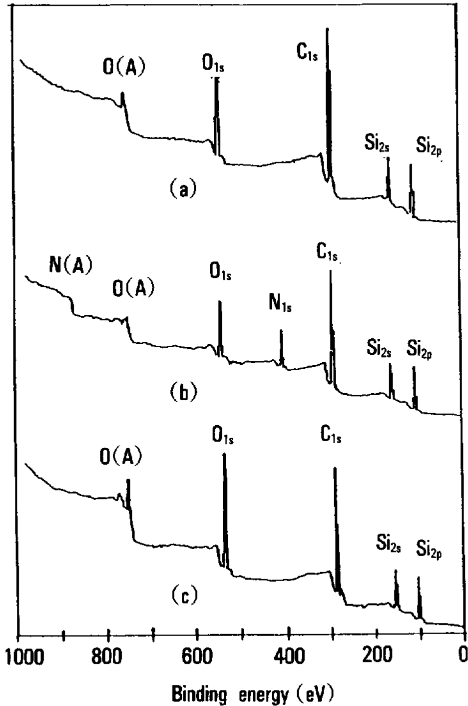


Fig. 9. Survey-scan XPS spectra of organosilicon plasma polymers formed at low input energy level : (a) TMS plasma polymer at W=30 watt, Fm=99.2 mg/min, P_o=200 millitorr, W/Fm=18.1 MJ/Kg, (b) HMDSIZ plasma polymer at W=30 watt, Fm=146.2 mg/min, P_o=200 millitorr, W/Fm=12.3 MJ/Kg, (c) HMDSIO plasma polymer at W=30 watt, Fm=142.6 mg/min, P_o=200 millitorr, W/Fm=12.6 MJ/Kg.

structure by varying the input energy level can be clearly explained by this reaction model.[18a] According to eq 1, the chemical structure of the plasma polymer is thought to be controlled by the activation pattern of a monomer in a discharge state. Since the activation of a monomer molecule into reactive fragments in a plasma should be related to the specific energy received per unit molecule (W/Fm), the control of the chemical structure by this parameter is well rationalized. The chemical structure of plasma polymer (Fig. 3) and its variation as a function of W/Fm (Fig.'s 4-6) readily suggest that the activation reaction possibly occurs by the fragmentation of Si-C, C-H, and N-H bonds of organosilicon molecule, and also that the increase of W/Fm possibly enhances the number of fragmented bonds per molecule in the activation step, leading to the enhanced character of cross-linked structure in the deposited plasma polymer. In fact, the plasma polymer formed at a relatively

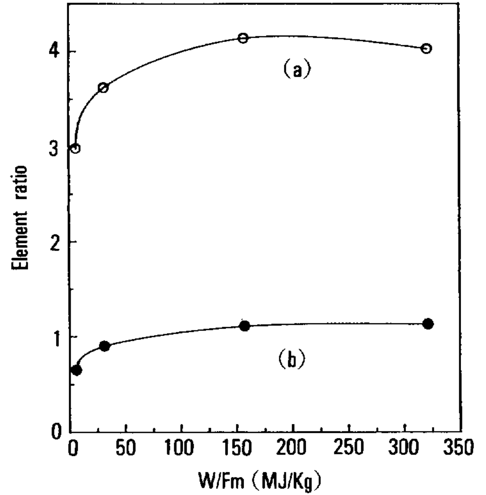


Fig. 10. Element ratio of (a) C/Si and (b) O/Si determined from the high-resolution XPS spectra of TMS plasma polymer as a function of W/Fm.

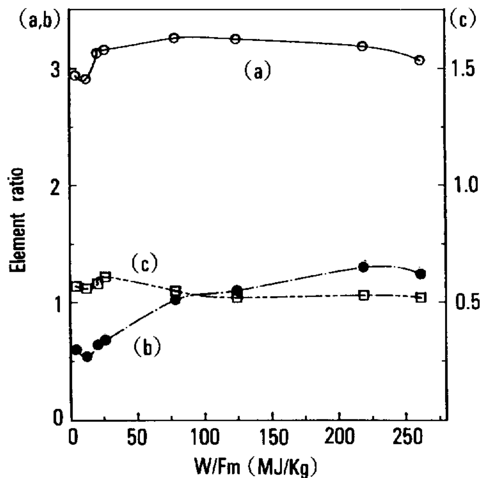


Fig. 11. Element ratio of (a) C/Si, (b) O/Si, and (c) N/Si determined from the high-resolution XPS spectra of HMDSIZ plasma polymer as a function of W/Fm.

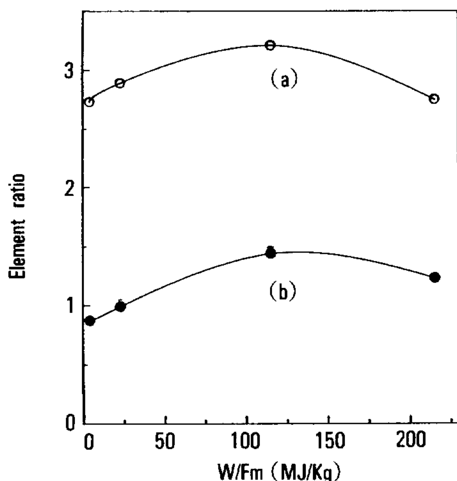


Fig. 12. Element ratio of (a) C/Si and (b) O/Si determined from the high-resolution XPS spectra of HMDSIO plasma polymer as a function of W/Fm.

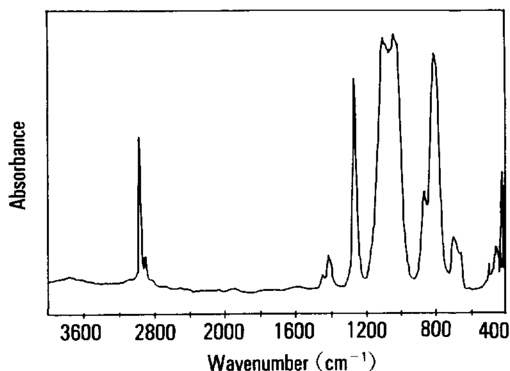


Fig. 13. FTIR spectrum of polydimethylsiloxane.

low W/Fm (< 30 MJ/Kg) is a very soft, polymer-like film which contains a large amount of Si-CH_3 group (Fig. 3). These groups can also be found in the spectrum of linear polydimethylsiloxane (Fig. 13), although it does not contain any discernible Si-H group. However, following the increase of W/Fm, the plasma polymer becomes gradually denser (also see Fig. 2 of Part II)[18b] and its chemical structure is no more similar to that of linear polymer (see Fig.'s 4-6). The monotonic increase of CH_2/CH_3 (Fig. 7) and Si-H/Si-CH_3 (Fig. 8) ratio with increasing W/Fm indicates the progressive enhancement of C-H or Si-C bond scissions per molecule in the activation step and explains the densification of the chemical structure.

At low W/Fm, the element ratio of Si to C of the plasma polymer determined from XPS measurements (Fig.'s 10-12) is initially less than that of monomer (4 for TMS, 3 for HMDSIZ and HMDSIO), however, this ratio increases with W/Fm as reported previously by Kokai et. al.,[29] and Coopes et. al.,[30] for TMS and HMDSIO plasma polymer, respectively. At present, this behavior is thought to originate from relatively low bond energy of Si-C (3.34 eV) compared to that of C-H (4.30 eV) bond. Thus, at low W/Fm, Si-C bond scission might be more probable than the C-H scission which initially lowers the C/Si ratio of plasma polymer below that of monomer. However, with subsequent increase of W/Fm, the role of C-H scission increases and therefore elevates the C/Si ratio. Then, at the much higher W/Fm level the ratio decreases again probably due to the severe sputtering effect of deposited polymer. The steady increase of O/Si ratio with W/Fm shown in the TMS and HMDSIZ plasma polymer also seems to support the activation growth nature of plasma polymerization since the oxygen in the plasma polymer, prepared from the monomers which does not contain oxygen, is generally believed to be incorporated through the post-plasma reaction of the trapped radicals with atmospheric oxygen or water.[1b] The constancy of N/Si ratio upon variation of W/Fm suggests that the Si-N bond scission is difficult to be involved in the activation process of the plasma polymerization due to the relatively high bond energy (4.61 eV) and the inorganic character of this bond. The plasma polymers obtained at a very high W/Fm (> 200 MJ/Kg) are extremely dense to be scraped out by razor blade and their FTIR spectra (Fig.'s 4-6 (d)'s) show negligible absorption of intact Si-CH_3 group (1253 cm^{-1}). These spectra also lack the appreciable absorption of C-H stretching and only reveal the broad absorption due to the skeletal stretching of inorganic Si-C (800-825 cm^{-1}), Si-N (800-900 cm^{-1}), and Si-O (1100-1000 cm^{-1}) which

were observed in the FTIR spectra of silicon carbide (SiC),[31] silicon nitride (SiN),[32] and silicon dioxide (SiO_2),[31] respectively. Thus, at this severe W/Fm conditions we obtain the plasma polymer whose structure seems to be similar to the inorganic material composed of tetrahedrally bonded covalent elements of Si and C, N, or O, depending on the chemical nature of monomers.

In conclusion, the chemical structure of organosilicon plasma polymer was uniquely controlled not only by the structure of monomers, but also by the input energy level (W/Fm) of plasma reaction. Generally, the plasma polymer formed at a fairly low W/Fm (< 30 MJ/Kg) was a very soft, polymer-like film containing a large amount of Si-CH_3 group in its structure. However, with increasing W/Fm, the structure became gradually denser with less organic groups, and finally approached the almost inorganic structure at the W/Fm of higher than 200 MJ/Kg. SiC-like structure was obtained in the TMS plasma polymer, SiC/SiN-like structure was obtained in the HMDSIZ plasma polymer, and SiC/SiO_2-like structure was obtained in the HMDSIO plasma polymer in good accordance with the chemical structure of those monomers.

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