

## 유기실리콘화합물의 플라즈마 중합에 관한 연구 : 3. 플라즈마 중합막의 막성장 속도론

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## Plasma Polymerization of Organosilicon Compounds : 3. Overall Kinetics of Plasma Polymer Deposition

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**요약 :** 유기실리콘 화합물의 플라즈마 중합에 있어 중합막의 막성장 속도에 관한 총괄 속도식을 간단한 활성화 성장기구 모델로부터 유도, 제안하였다. 실험에 의해 측정된 중합막의 막성장 속도는 제안 속도식에 의해 잘 설명되었다. 특히, 제안 속도식의 플라즈마 중합 에너지 조건 (W/Fm)에 의한 중합막의 막성장효율의 제어는 W/Fm에 의한 화학구조 및 물성의 변화와 긴밀한 관계가 있음을 알 수 있었다.

**Abstract :** The overall kinetic equation for the deposition rates of organosilicon plasma polymer was derived from the activation growth model of plasma polymerization. Regression analyses of the experimental deposition rates supported the proposed equation. The role of input energy level W/Fm in controlling the deposition yield of monomer was closely related to the observed changes of structure and properties of plasma polymer.

### INTRODUCTION

In Parts I and II of this study<sup>1,2</sup> it was shown that the chemical structure and physical properties

of organosilicon plasma polymer could be controlled by the input energy level (W/Fm) of plasma reaction according to the activation growth nature of that process. It was also shown that the plasma

polymer represented a new class of material whose structure and properties extended over the intermediate range between the polymeric and inorganic material.<sup>3</sup> Thus, this unique process of thin film formation seems to extend the range of material selection in many technological applications.<sup>4</sup> Due to this enhanced range of molecular design and also to the excellent thin film properties, the plasma polymerization process has received considerable attention. Accordingly, there is an ever increasing interest in the mechanism and kinetics of plasma polymerization deposition.<sup>3</sup> However, the plasma reactions are extremely complex and moreover dependent on too many experimental parameters to be clearly understood by the theoretical reasoning.<sup>3</sup> Therefore, many investigators have attempted to derive the kinetic equation of plasma polymer deposition with the postulated mechanism of plasma polymerization, usually the conventional chain propagation mechanism.<sup>5-8</sup> Although those kinetic equations seemed to partly explain the observed deposition rates in terms of some reaction parameters, the chain propagation mechanism used for the derivation of equation is not justified since it cannot account for the most important aspect of plasma polymerization, namely, the control of chemical structure by reaction parameters. Recently, Yasuda and Wang<sup>9</sup> proposed a simple empirical equation of plasma polymer deposition based on the "rapid step growth polymerization (RSGP)"<sup>3</sup> (activation growth<sup>10</sup>) mechanism which seems to be the most likely model of plasma polymerization as also shown in Parts I and II of this study.<sup>1,2</sup> Many investigators have reported the supporting results for this equation, however, experimental results are yet insufficient and occasionally inconsistent to draw general conclusion.<sup>3</sup> In the present work, we examined the deposition rates of three organosilicon plasma polymers in terms of reaction parameters  $W$  and  $F_m$  which played an important role in controlling the chemical structure and physical properties.<sup>1,2</sup> Through the analysis of deposition rates using the activation growth concept and the mass balance equation

proposed very recently by Yeh and coworkers,<sup>11</sup> a new kinetic equation was derived which seems to possess general applicability.

## EXPERIMENTAL

### Plasma Polymerization

The detailed description of the plasma reactor and the general procedure of plasma polymerization should be referred to the experimental section of Part I.<sup>1</sup>

### Deposition Rates

The deposition rates of tetramethylsilane (TMS), hexamethyldisilazane (HMDSIZ), and hexamethyldisiloxane (HMDSIO) plasma polymer were examined in terms of discharge power ( $W$ ) and mass flow rate ( $F_m$ ). For each monomer, four different  $W$  (typically, 10, 30, 50, 100 watt) and seven different  $F_m$  were employed to the twenty-eight individual reaction conditions specified by  $W$ ,  $F_m$ . A pair of slide glasses (Clay Adams, No 3058) masked with thin cover slips were used as the substrate on the lower electrode. After the deposition of plasma polymer, the step-heights at the six radial positions (5, 13, 20, 30, 38, 45mm from the center of lower electrode) were measured using a Talysurf 10 (Taylor-Hobson). The average deposition rate on the lower electrode ( $DR : \text{\AA}/\text{min}$ ) was calculated from the six local deposition rates (step-height/deposition time). The mass deposition rate ( $DR_m : \text{mg}/\text{min} \cdot \text{cm}^2$ ) was then calculated from  $DR$  and the evaluated density of that plasma polymer at each  $W$ ,  $F_m$  conditions.

## RESULTS AND DISCUSSION

Fig.'s 1-3 show the variations of  $DR_m$  according to the changes of  $W$  and  $F_m$  for the organosilicon monomers TMS, HMDSIZ, and HMDSIO respectively. By the gradual increase of  $F_m$  at a fixed  $W$ ,  $DR_m$  initially increases almost linearly with  $F_m$  then decreases after passing the  $DR_m$  maxima. Obviously, such behavior is apparent at all the  $W$  levels and monomers examined. It is also apparent

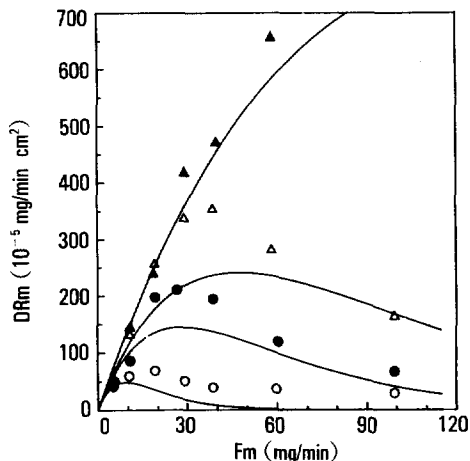


Fig. 1. Deposition rate (DRm) of TMS plasma polymer as a function of monomer flow rate (Fm) at 10 watt (○), 30 watt (●), 50 watt (△), and 100 watt (▲) discharge power level, respectively. The lines were drawn according to eq 4 with C and Ea values of Table 1.

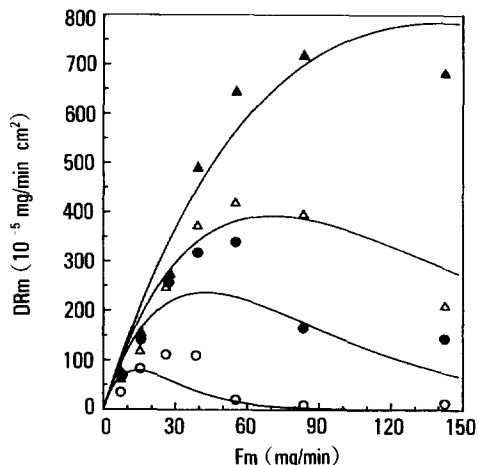


Fig. 3. Deposition rate (DRm) of HMDSIO plasma polymer as a function of monomer flow rate (Fm) at 10 watt (○), 30 watt (●), 50 watt (△), and 100 watt (▲) discharge power level, respectively. The lines were drawn according to eq 4 with C and Ea values of Table 1.

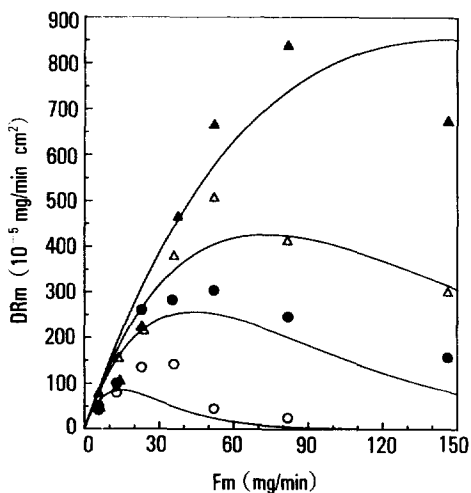


Fig. 2. Deposition rate (DRm) of HMDSIZ plasma polymer as a function of monomer flow rate (Fm) at 10 watt (○), 30 watt (●), 50 watt (△), and 100 watt (▲) discharge power level, respectively. The lines were drawn according to eq 4 with C and Ea values of Table 1.

that the value of Fm which yields the DRm maxima shifts to the higher Fm when the W level is raised. These observations are not peculiar to the organosilicon monomers examined in this study. Many workers already reported the same behavior in the plot of deposition rate versus flow rate.<sup>3</sup> Therefore, we were strongly tempted to investigate the possible origin of this kinetic result based on the activation growth mechanism of plasma reaction,<sup>1-3,10</sup> since the significant changes in the chemical structure (Part I)<sup>1</sup> and physical properties (Part II)<sup>2</sup> of plasma polymer could be clearly explained by this mechanism.

Recently, Yeh and co-workers<sup>11</sup> investigated the fundamental mass balance in the plasma polymerization system and found that the empirically obtainable average local deposition rate  $\overline{DRm}$  having a unit dimension of mass/area · time is the function of three influencing factors,  $Y_p$ ,  $x'/S$ , and Fm, where  $Y_p$  is the yield of the plasma polymer deposition,  $x'$  is the fraction of feed-in monomer that flows in the glow discharge zone, S is the area of the surface on which plasma polymer is deposited

(thus,  $\overline{DRm}$  times S is the integrated polymer deposition rate), and Fm is the total mass flow rate of monomer.

$$\overline{DRm} = Y_p (x'/S) F_m \quad (1)$$

The yield of plasma polymer deposition ( $Y_p$ ) means the fraction of feed-in monomer that takes part in the formation of plasma polymer. Therefore,  $Y_p$  is the factor that is primarily related to the mechanism of plasma polymerization, on the other hand,  $x'/S$  is the geometrical factor of plasma reactor and Fm is the controllable parameter. From eq 1, it is apparent that  $Y_p$  is proportional to  $\overline{DRm}/F_m$  if  $x'/S$  is kept constant. Recently, Yasuda and co-workers found that  $\overline{DRm}/F_m$ , thus  $Y_p$ , is controlled by the input energy level  $W/F_m$ .<sup>3,11</sup> Generally, two domains of plasma polymerization were distinguished in the  $\overline{DRm}/F_m$  versus  $W/F_m$  plot, namely, energy-deficient region where  $\overline{DRm}/F_m$  increased almost linearly with  $W/F_m$  and monomer-deficient region where it leveled to some constant value. This means that the  $\overline{DRm}$  is controlled by W in the former region and by Fm in the latter region, which is the empirical kinetics of plasma polymer deposition proposed by Yasuda

and Wang.<sup>9</sup> Just the same results are also observed in our plasma polymerization experiments of three organosilicon monomers as shown in Fig.'s 4-6, respectively. At the energy-deficient regions (approximately less than  $10^2$  MJ/Kg) an order of magnitude increase in  $\overline{DRm}/F_m$  with  $W/F_m$  is clearly shown, then, at the monomer-deficient region (higher  $W/F_m$  region)  $\overline{DRm}/F_m$  levels to some constant value. Thus, our experimental results also confirm the kinetics proposed by Yasuda and Wang,<sup>9</sup> however, from the viewpoint of activation growth mechanism of plasma polymerization, it is not clear why the plasma polymer deposition should be described by distinguishing the two separate domains.

In Parts I and II of this study,<sup>1,2</sup> it was shown that the plasma polymerization proceeds possibly through the repeated activation and recombination steps of molecular bonds. Most importantly, the degree of activation per molecule was thought to be controlled by the input energy level ( $W/F_m$ ) of plasma reaction since we could explain the systematic changes of structure and properties in terms of that parameter. According to the activation growth scheme shown as eq 1 in Part I,<sup>1</sup> it is apparent

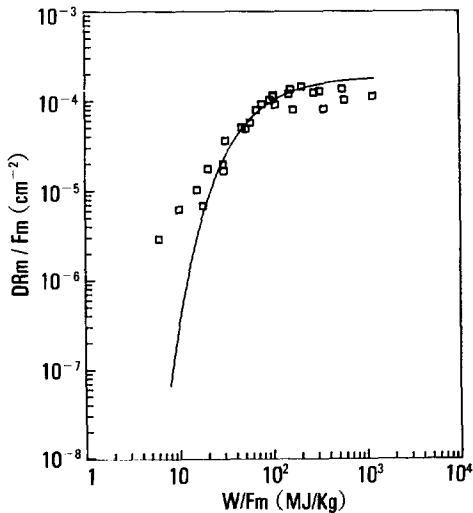


Fig. 4.  $\overline{DRm}/F_m$  versus  $W/F_m$  plot for the plasma polymerization of TMS. The line was drawn according to eq 5 with C and  $E_a$  values of Table 1.

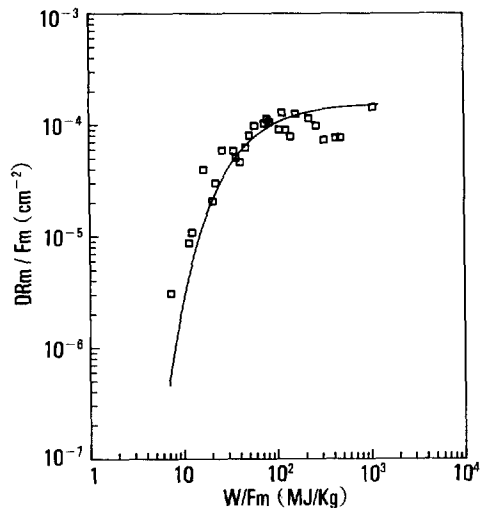


Fig. 5.  $\overline{DRm}/F_m$  versus  $W/F_m$  plot for the plasma polymerization of HMDSIZ. The line was drawn according to eq 5 with C and  $E_a$  values of Table 1.

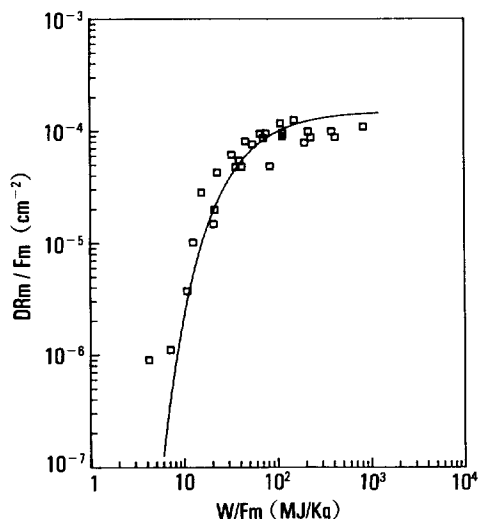


Fig. 6. DRm/Fm versus W/Fm plot for the plasma polymerization of HMDSIO. The line was drawn according to eq 5 with C and Ea values of Table 1.

that the activation of a molecule into reactive species (which is controlled by W/Fm as above mentioned) is the necessary condition for that molecule to participate in the formation of plasma polymer. This means the yield of deposition  $Y_p$  should also be controlled by the activation reaction, thus, by the input energy level W/Fm as actually shown in Fig's 4-6. Here, it seems reasonable to consider the activation step as an "activated process" driven by the specific energy supplied per mole of monomer. Then,  $Y_p$  is simply expressed in terms of W/Fm as shown in eq 2 since the value of W/Fm is just the specific energy per mass of monomer in the plasma reactor.

$$Y_p = \exp\left(-\frac{E_a}{W/Fm}\right) \quad (2)$$

By substituting  $Y_p$  into eq 1, we obtain an equation of plasma polymer deposition.

$$\overline{DRm} = \exp\left(-\frac{E_a}{W/Fm}\right) \left(\frac{x'}{S}\right) Fm \quad (3)$$

Experimentally, we used a flow configuration that forced monomer vapor to flow through interelectrode glow zone, thus, it is not unreasonable to

assume the value of  $x'$  as 1 and that of S as inner surface area of reactor (ca. 2000 cm<sup>2</sup>). However, the exact value of  $\overline{DRm}$  in eq 3 could not be determined because it is almost impossible to measure local deposition rates at all the locations in a whole reactor. We only measured six local deposition rates on the lower electrode and thus obtained the average value of them as DRm (in unit of mg/min · cm<sup>2</sup>). Generally, it was observed that the local deposition rate on lower electrode was much higher than that on the reactor wall. Thus, we expect that the changes of  $\overline{DRm}$  as a function of operational parameters can be well monitored by the measured value of DRm although the magnitude of DRm might be much larger than  $\overline{DRm}$ . In this case, eq 3 can be rewritten as eq 4 to correlate the measured deposition rates with operational parameters W and Fm : where C comprises both  $x'/S$  term and the unspecified scale factor of  $\overline{DRm}/DRm$  ratio.

$$DRm = C \exp\left(-\frac{E_a}{W/Fm}\right) Fm \quad (4)$$

Then, from eq 4, DRm/Fm is simply related to W/Fm as follows.

$$\frac{DRm}{Fm} = C \exp\left(-\frac{E_a}{W/Fm}\right) \quad (5)$$

In fact, the lines shown in Fig's 4-6 were drawn according to eq 5 with C and  $E_a$  values obtained by the regression analysis of whole data set of respective monomer using the computer program for a multi-variable nonlinear regression which minimizes the sum of the squares difference (see Table 1). It seems that the lines approximate the experimentally obtained results closely and visualize the nearly linear increase of DRm/Fm at lower W/Fm region and leveling at higher W/Fm region as was generally observed in the plasma polymerization of many organic or organometallic compounds.<sup>3</sup> Thus, it seems likely that the two domain concept in the DRm/Fm versus W/Fm plot is just the simplified expression of eq 5. Furthermore, the lines in Fig's 1-3 were also drawn according to the

**Table 1.** Result of Regression Analysis by Using eq 4

Monomer	Ea (MJ/Kg)	C (cm <sup>-2</sup> )	φ (MJ/Kg)*
TMS	63.6	1.39 × 10 <sup>-4</sup>	70.2
HMDSIZ	40.8	1.58 × 10 <sup>-4</sup>	62.8
HMDSIO	42.5	1.51 × 10 <sup>-4</sup>	62.8

\* specific bond energy =  $\Sigma(\text{bond energy})/\text{molecular weight}$

eq 4 at four W levels for respective monomer. It is also apparent that the lines approximate the experimental data closely and visualize the generally observed trends of DRm maxima at certain Fm value and their shift to higher Fm value with increasing W level. Simple mathematical treatment (differentiation of eq 4 with respect to Fm) allows us to obtain the specific condition of DRm maxima, namely, the input energy level (W/Fm) at the DRm maxima equals the value of Ea. Interestingly enough, the apparent activation energy (Ea) of plasma polymerization seems to be closely related to the average bond energy (φ) of molecule as shown in Table 1.

From these considerations, it is concluded that the generally observed deposition behavior and also the two domain concept of plasma polymerization could be explained by the simple kinetic equation of activation growth reaction. However, it should be noted that the proposed eq 4 (or 5) accounts only for the basic mechanism of plasma polymerization without considering the more complicated problems of plasma polymerization, such as

the hydrogen yield,<sup>3</sup> competitive ablation with deposition,<sup>3</sup> or substrate temperature.<sup>9</sup> Much work remains to be done in this area, and we are currently doing some of these topics.

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