Pulsed RF Plasma Graft-polymerization of Acetylene & Styrene

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Pulsed RF plasma graft-polymerized styrene revealed sub nm pattern delineated by an electron-beam. The polymerization by the boxed type reactor was referred to radical mechanism from the theoretical analysis with using acetylene even if the capacitive coupled reactor was used. The details of pulsed plasma polymerization rate were calculated theoretically and showed good co-relation with the experimental results.

Keywords: pulsed RF plasma graft-polymerization, acetylene, styrene, radical reaction, theoretical calculation of growth rate

1. Introduction
Pulsed RF plasma polymerizations had been studied variously [1,2], where the pulse modification was performed in the level of m-sec. Among several active elements of charged particles and/or radicals in the plasma, mostly charged particles were control at the period of pulse modulation. The lifetime of charged particle is short, but the lifetime of radical is sometime more long. In the case of material processes, the radicals are the most important species in the processes. Among the organic radicals, some of them have very long lifetime like as a second or more depending on the molecular structures. In this work, the pulse modulation of RF power at 13.56 MHz is performed as 0.1 sec ON and 0.9 sec OFF with box type reactor [3] as shown in Fig. 1, which has parallel plate discharge electrodes with the area of $10 \times 6 \text{ cm}^2$ and gap distance of 1.5cm and the reaction area is limited by the insulating Teflon walls on both side along gas flow. The reaction gas is introduced through small hole of 0.3 mm $\phi$ in the Teflon plate. Therefore the reaction gas is estimated to flow uniformly in the reaction area.

Fig. 1. Box type pulsed RF plasma reactor with the discharge electrode area ($10 \times 6\text{cm}^2$) and gap distance of 1.5cm

Reactions of several monomers in the box type reactor were studied [3] and graft polymerization was discussed in the long OFF time
period. Therefore the pulsed RF plasma polymerization means that 0.1 sec RF plasma polymerization and 0.9 sec graft-polymerization were repeated in the deposition process.

In the plasma polymerization, there are two models of radical and ionic reaction \[4,5,6\]. In the capacitive coupling reactor, the ionic species are predominant because the deposition rate on the discharge electrode is largest compared to the other deposition on the solid surface in the plasma.

Pulsed RF plasma polymerized styrene was evaluated as a resist for the nanometer pattern fabrication \([7]\). In this paper, the resist properties are discussed in the relation with the reaction mechanism. In order to confirm the radical model, pulsed RF plasma polymerization of acetylene will be discussed with using the theoretical calculations.

\[
R_{gn}'+M_g \rightarrow R_{gn+1}' \quad \cdots(2).
\]

The monomer and radical are adsorbed on to the substrate as,
\[
S + M_g \rightarrow M_s \quad \cdots(3)
\]
\[
S + R_{gn}' \rightarrow R_{sn}' \quad \cdots(4).
\]

The radical is propagated on the substrate by reacting with the monomer in gas phase or adsorbed on the substrate as,
\[
R_{sn}'+M_g \rightarrow R_{sn+1}' \quad \cdots(5)
\]
\[
R_{sn}'+M_s \rightarrow R_{sn+1}' \quad \cdots(6)
\]

Then the radicals reacted to form polymer, and the polymerization is finished as,
\[
R_{gm}' + R_{gn}' \rightarrow P_{gm+n} \quad \cdots(7)
\]
\[
R_{sm}' + R_{sn}' \rightarrow P_{sn+n} \quad \cdots(8)
\]
\[
R_{sn}' + R_{sn}' \rightarrow P_{sn+n} \quad \cdots(9)
\]

If the electron collides onto the polymer, the polymer will become the radicals as,
\[
e + P_s \rightarrow R_{sn}'+R_{sn}' \quad \cdots(10)
\]
\[
e + P_s \rightarrow R_{sn}'+R_{sn}' \quad \cdots(11)
\]

In the plasma, these reactions will be repeated.

2. Theoretical Calculation of Pulsed RF Plasma Polymerized Acetylene in the Box type Reactor
2.1 Radical Reactions\[8,9\]

Box type pulsed RF plasma reactor of Fig. 1 is simplified as shown in Fig. 2 for the discussion of reaction. The total gas flow rate is \(Q\), a partial volume in the reactor is \(\delta V\), and the gap distance between the electrodes is \(h\) in the figure. Also \(e\) is electron, \(M\) is monomer, \(R\) is radical, \(P\) is polymer, \(S\) is substrate and suffix of \(g\) and \(s\) mean the gas phase and substrate. When the high energy electron collide on the monomer, radical is formed as following,
\[
e + M_g \rightarrow 2R_g' + e \quad \cdots(1).
\]

The radical is propagated by reaction with the monomer as

\[
R_{gn}'+M_g \rightarrow R_{gn+1}' \quad \cdots(2).
\]

The monomer and radical are adsorbed on to the substrate as,
\[
S + M_g \rightarrow M_s \quad \cdots(3)
\]
\[
S + R_{gn}' \rightarrow R_{sn}' \quad \cdots(4).
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The radical is propagated on the substrate by reacting with the monomer in gas phase or adsorbed on the substrate as,
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In the plasma, these reactions will be repeated.

2.2 Calculation of Deposition Rate and Deposited Mass

The reaction in a reactor with parallel plate electrodes as shown in Fig. 2 is considered here. The radical density is calculated during the gas flow between the electrodes. However the variation of radical density caused on the termination or dissociation of polymers is supposed to be small under this condition. If the reactions of (1), (2), and (4) are supposed to be preeminent, the following equation is obtained.

The increase of radical density in the volume \(\delta V\) in the plasma is the remained density which was obtained by deleting the consumed radical from the produced radical. The following equation is obtained as,
\[
\frac{d(Q/R_g)}{dV} = 2k_1[e][M_g] - \frac{2}{\hbar}k_4[R'_g][S] \quad \cdots (12).
\]

In the same manner, the increase rate of monomer density in the volume \(dV\) is the remained density which was obtained by deleting the changed to radical (1) and consumed by the polymerization (2) as,
\[
\frac{d(Q[M_g])}{dV} = -k_1[e][M_g] - k_2[R_g][M_g] \quad \cdots (13)
\]
where, \(k_1, k_2, k_4\) are reaction constants of (1), (2) and (4), respectively. Here reaction probability between radical and monomer is small enough compared to the probability of monomer activation by electron, therefore equation (13) second paragraph is neglected. If \(Q\) is constant, the time of gas exposed to the plasma is \(\tau = V/Q\), the differential equation becomes as,
\[
\frac{d[R_g]}{d\tau} = 2k_1[e][M_g] - \frac{2}{\hbar}k_4[R_g][S] \quad \cdots (14)
\]
\[
\frac{d[M_g]}{d\tau} = -k_1[e][M_g] \quad \cdots (15)
\]
By solving these equations, following equations will be obtained as,
\[
[M_g] = [M_g]_0 \exp(-a\tau) \quad \cdots (16)
\]
\[
[R_g] = [M_g]_0 \frac{2a}{(a-b)} \left\{ -\exp(-a\tau) + \exp(-b\tau) \right\} \quad \cdots (17)
\]
where \([M_g]_0\) is monomer density at \(\tau = 0\), \(a = k_1[e]\), and \(b = (2\hbar/k_4[S])\) This is the case that gas flow time is short, \(\tau\) is revealed as the linear relation at \(\tau = 0\), therefore the equation (17) is simplified as the following equation as,
\[
[R_g] = 2[M_g]_0 a\tau \quad \cdots (18).
\]
The increased mass of radical molecule \(m\) is obtained by polymerization equation (2).
Polymerized radical molecule density is decrease with time, but the molecular mass is increased with time.
If the time is short, the mass \(m\) is supposed to increase with time linearly as same as equation (18). Then the equation become as,
\[
m(t) = m_0 + ct \quad (c = \text{const}) \quad \cdots (19)
\]
The radical growth rate per unit volume in time \(\tau\) become as \(d[R_g]/d\tau\), whereas the mass of deposited volume is shown as,
\[
\bar{m}(\tau) = \frac{1}{[R_g]} \int_{t=0}^{\tau} \frac{d[R_g]}{dt} m(\tau - t) dt \quad \cdots (20)
\]
With using equation (18) and (19),
\[
\bar{m}(\tau) = m_0 + \frac{c}{2} \tau \quad \cdots (21).
\]

Fig. 3. Deposited thickness dependence on the distance from the gas inlet.

If discharge period from the start is \(t\), the time of gas exposed to the plasma become \(\tau\) at the position \(x\), \(\tau\) become as,
\[
\tau = \begin{cases} 
  t & (t < \frac{x}{v}) \\
  \frac{x}{v} & (t > \frac{x}{v})
\end{cases} \quad \cdots (22).
\]
The adsorbing rate becomes proportional to the radical density as \( K_R [R^*_{x}] \). The deposition mass rate \( r \) becomes as,
\[
r = \bar{m}(t)K_R [R^*_{x}]
\]

(23).

This is obtained from the equations (20), and (22).
\[
r = \begin{cases} 
K_R [M_g]_o a(2m_0 t + c t^2) & (t < \frac{x}{v}) \\
K_R [M_g]_o a\left\{2m_0 \frac{x}{v} + c(\frac{x}{v})^2\right\} & (t > \frac{x}{v})
\end{cases}
\]

(24).

The deposition rate increase proportionally to the second order in the period of \( 0 \sim x/v \) then it saturated. The saturated value is proportional to the second order of distance from the gas inlet. Therefore the deposition rate \( P(t) \) is obtained by integrating as,
\[
P(t) = \begin{cases} 
K_R [M_g]_o a\left\{m_0 (\frac{x}{v})^2 + \frac{c}{3} (\frac{x}{v})^3\right\} & (t < \frac{x}{v}) \\
K_R [M_g]_o a\left\{m_0 (\frac{x}{v})^2 + \frac{c}{3} (\frac{x}{v})^3\right\} + \left\{2m_0 \frac{x}{v} + c(\frac{x}{v})^2\right\}(t - \frac{x}{v}) & (t > \frac{x}{v})
\end{cases}
\]

(25).

2.3 Comparison with experimental results

Because the pulsed plasma used had the repeatability of T. the discharge period in the unit time is \( \alpha T \) and pulse number is \( n \). The gas flow velocity was 81.6 cm/s, therefore \( \alpha T > x/v \) at all experimental points. The total deposited mass \( P_{at} \) becomes as,
\[
P_{at} = n P(\alpha T)
\]
\[
= nK_R [M_g]_o a\left\{m_0 (\frac{x}{v})^2 + \frac{c}{3} (\frac{x}{v})^3\right\} + \left\{2m_0 \frac{x}{v} + c(\frac{x}{v})^2\right\}(\alpha T - \frac{x}{v})
\]

(26).

Therefore \( P_{at} \) is proportional to third order function. The result could be fitted to the experimental result as shown in Fig. 3. There is good correlation between the theoretical result and experimental results.

The deposition rate measured by quartz sensors show the average value at 5.5 cm from the gas inlet. The growth rate \( \bar{r} \) becomes as,
\[
\bar{r} = \frac{P(\alpha T)}{T} = K_R [M_g]_o a\left[-\frac{2}{3} c(\frac{x}{v})^3 + m_0 (\frac{x}{v})^2\right] \frac{1}{T} + \alpha\left\{c(\frac{x}{v})^2 + 2m_0 \frac{x}{v}\right\}
\]

(27).

3. Pulsed RF Plasma Polymerized Styrene in the Box-type Reactor

Pulse RF plasma polymerization of styrene was performed at a pressure of 0.5 Torr, a gas flow rate of 30 SCCM, a discharge power of 10 W, a pulse modulated as 0.1 sec ON and 0.9 sec OFF and a pulse number of 1000. The deposited film thickness was about 60 nm. The properties as a resist was evaluated by the lithography process. The hp 50 nm pattern was delineated at 50 kV and 1 nA by using the electron beam patterning machine (JEOL, JBX-6000SG). The pattern was developed at 1 sec using hexane. The delineated pattern was successfully developed [7]. The resist sensitivity was evaluated to be 400 \( \mu \) C/cm\(^2\) as shown in Fig. 5, which is higher than that (1000-10,000 \( \mu \) C/cm\(^2\)) of conventional polystyrene (mass of 17,500-800) [10]. The result is quite strange because the plasma-polymerized film has usually cross-linked molecular structure which means lower sensitivity. The high sensitivity was referred to the special molecular structures, which were composited with the grafted molecules to Si wafer and the lower molecular weight molecules. The high sensitivity was supposed to be caused on the cross-linking between these two kind molecules at the small dose rate to fix the lower molecular weight molecules to the substrate, because the
anchored molecules to the Si wafer substrate were not flowed with the developing solvent. The small molecular weight molecules formed by the pulsed RF plasma process are supposed to be formed by the radical mechanism in the discharge OFF period.

4. Conclusion
Pulsed RF plasma polymerization was supposed to be performed by the radical mechanism even if the capacitive coupled reactor enhances the ionic molecules to bombard onto the deposited film surface. It is expected that the pulsed RF plasma process can be applied to develop the new materials.

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