

Influences of the System Pressure and the Substrate Temperature on Plasma Polymers

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Synopsis

Plasma polymerizations of aluminium-acetylacetonate (Al—AcAc) complex using a magnetically enhanced plasma reaction system were investigated as functions of the system pressure and the substrate temperature. The system pressure and the substrate temperature rather than the RF power played an important role in plasma polymerization reactions. The high system pressure and the high substrate temperature led to bond scission of monomers to yield plasma polymers rich in aluminium moieties. The chemical composition of plasma polymers prepared from Al—AcAc complex was discussed from spectroscopic results with FT-IR and XPS.

INTRODUCTION

Plasma polymerization is a process which produces a variety of functional organic thin films. The technique is applied for modification of surface properties such as hydrophilicity, hydrophobicity, surface hardness, biocompatibility, etc. The polymer-formation process in plasma polymerization is different in reaction mechanism from that in conventional polymerization.

Yasuda¹ has recently discussed the polymerization and deposition mechanism in plasma polymerization process, and proposed a new concept, rapid step-growth polymerization (RSGP) mechanism. This concept includes the activation of starting molecules by plasma, the formation of monovalent or divalent reactive species, the cross-cycle reaction between two reactive species, the collision of species against substrate surfaces, and the relaxation of kinetic energy of the species. The deposition of plasma polymers occurs when impinging species fail to leave the substrate surface by loss of kinetic energy or by the formation of chemical bonds. The RSGP aspect points out some similarities between the plasma polymerization and vacuum-evaporation technique, although plasma polymerization process involves some chemical reactions in a plasma zone.

The vacuum-evaporation technique includes a sublimation and a condensation process.² The condensation process where the film formation occurs, is related with a balance among the adsorption of sublimated molecules at the substrate surface, the surface-diffusion of the adsorbed molecules, and the secession of the adsorbed molecules from the substrate surface.³ Therefore the condensation process is mainly controlled by a magnitude of energy levels that the molecules reaching the substrate surface have and that the molecules are

lost at the substrate surface. These energy levels may be related to both of the system pressure and the substrate temperature.

It is well known that the movement and kinetic energy of molecules present in vacuum are evaluated by the mean free path, which is determined by the system pressure.³ The mean free path, for instance, is about 100 cm at a system pressure of 1×10^{-2} Pa, and is about 1 cm at 1 Pa.

From a point of view of energy balance, in this study, we investigate a plasma polymerization process. Influences of the system pressure and the substrate temperature on the chemical composition of deposited plasma polymers are examined by the elemental analysis, FT-IR spectroscopy, and XPS. And these influences are compared with influences by changing the RF power being a major factor in plasma polymerization reaction. Aluminium-acetylacetonate (Al—AcAc) complex was used in this study as a starting material for plasma polymerization. Plasma polymers prepared from metal-containing compound call an attention for application of a organic semiconductor, a chemical sensor, a solar cell, etc.⁴⁻⁶

EXPERIMENTAL

Plasma Polymerization

The apparatus used in this study for plasma polymerization was a capacitively coupled system (13.56 MHz)⁷ containing a parallel pair of electrodes, an electromagnetic coil, a furnace for monomer sublimation, and a vacuum system,

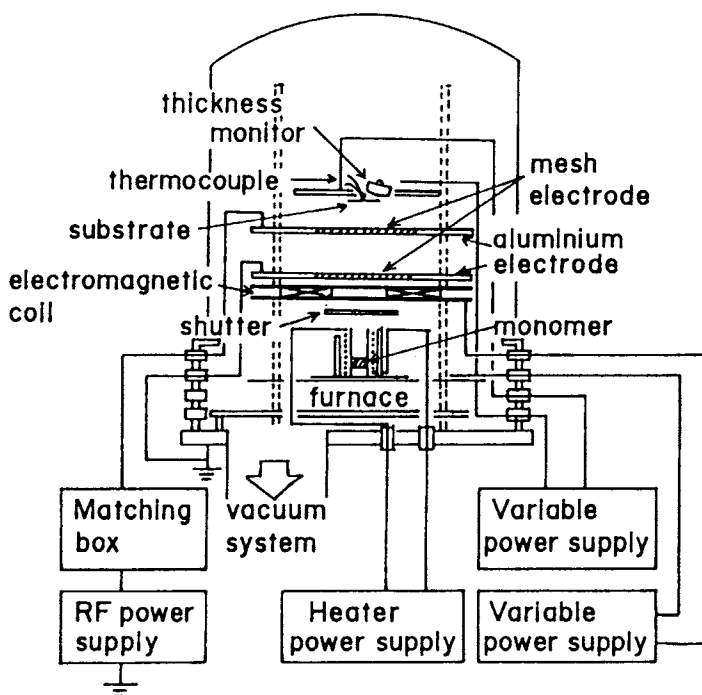


Fig. 1. Schematic illustration of a magnetically enhanced plasma reaction system.

as shown in Figure 1. The pair of plasma electrodes was a circular aluminium plate (30 cm in diameter) and a mesh plate (12 cm in diameter). The electromagnetic coil was positioned at 1.5 cm far under the aluminium electrode. A DC current of 20 A was circulated in the electromagnetic coil. The magnetic field generated by the electromagnetic coil was 5–150 G.

Mirror-polished, *n*-type Si(111) wafers (0.05 Ω cm), glass slides, and stainless steel sheets were used as substrates. The surface of the substrates was cleaned in substrate-cleaning solution (Semico Clean 56; Furuuchi Chem., Japan) by an ultrasonic cleaner for 15 min at room temperature, rinsed with ethanol, and air dried. The substrate was mounted on the substrate holder, which was positioned at 20 cm far from the monomer furnace. The substrate surface was cleaned by exposure of argon plasma (at 60 W at 0.13 Pa for 10 min) before initiating the plasma polymerization. The reaction system was evacuated to less than 8×10^{-4} Pa once again, and argon was introduced into the reaction chamber at 6.6×10^{-2} Pa. The RF power was turned on and at the same time Al–AcAc complex was sublimated from the furnace. The operating conditions for plasma polymerization were as follows: the system pressure was 2.6 – 2.6×10^{-2} Pa, the substrate temperature 10–550°C, the RF power 20–60 W, and the applied magnetic field 30 G.

The deposited rate was monitored with a quartz crystal monitor (ULVAC, CRTM-5). The temperature of the substrate was measured with a CA thermocouple.

IR and XPS Spectra

IR spectra of the plasma polymers deposited on glass slides and stainless steels were recorded with a JASCO fourier transform spectrometer FT/IR-3. A KBr or an ATR method was applied for IR measurement.

Plasma polymer films deposited on the silicon wafers were provided for the measurement of XPS spectra. XPS spectra were recorded with an ULVAC spectrometer 5400 employing $MgK\alpha$ exciting radiation at 400 W and 15 kV. The complex C_{1s} and O_{1s} spectra were subjected to curve-fitting procedure. A Gaussian distribution was assumed, and three parameters, the position, the height of the peak, and the full width at half-maximum (FWHM), were varied to correspond roughly to the observed spectra by using a computer program supplied by ULVAC. The FWHM value of each resolved curves was within 2 eV. Following sensitivity factors (S) were used to calculate the relative atomic concentration: $S(C_{1s}) = 2.96$, $S(O_{1s}) = 7.11$, and $S(Al_{2p}) = 2.34$.

RESULTS AND DISCUSSION

Influence of the System Pressure

The system pressure, as described in the introduction part, is related to kinetic energy, the mean free path of molecules present in vacuum. The mean free path (λ) of Al atoms can be calculated by Eq. (1)³

$$\lambda = 3.107 \times 10^{-18} \cdot T/P \cdot \delta^2 \text{ (cm).}$$

$$\delta = r + r' \tag{1}$$

where T is the absolute temperature (K), P is the pressure (Pa), and r and r' are the radius of gases (cm). For example, when an Al atom is evaporated in vacuum, the flying distance without a collision, the mean free path, is calculated according to Eq. (1) with $T = 300$ K, $r = r' = 1.5 \times 10^{-8}$ cm (Al atom). The mean free path is 5.2×10^{-3} cm at a system pressure of 2.6 Pa and 52 cm at 2.6×10^{-2} Pa. The calculation indicates that decreases in the system pressure mean increases in the mean free path (the kinetic energy). From such a point of the view, plasma polymerization reactions may be influenced by the system pressure.

Plasma polymerization was performed at a RF power of 60 W and an electric field of 30 G when the system pressure varied from 2.6 Pa to 2.6×10^{-2} Pa. Figure 2 shows the polymer deposition rate as a function of the system pressure. The deposition rate in performing the plasma polymerization at 2.6 Pa was $0.76 \mu\text{g}/\text{cm}^2 \cdot \text{min}$ and the deposition rate at 2.6×10^{-2} Pa was $7.3 \mu\text{g}/\text{cm}^2 \cdot \text{min}$ indicating that the system pressure is an important factor to control the polymer deposition.

Then how did the system pressure also influence on the chemical composition of the plasma polymers deposited? Plasma polymerization of Al—AcAc complex yielded light-yellow films when the system pressure changed from 2.6 Pa to 2.6×10^{-2} Pa. Figure 3 shows typical IR spectra of the plasma polymers as a function of the system pressure. Al—AcAc complex, as shown in Figure 3(a), showed absorption peaks at 491 cm^{-1} due to $\nu(\text{Al—O})$ and $\nu(\text{C—CH}_3)$; 579 cm^{-1} due to ring deformation and $\nu(\text{Al—O})$; 687 cm^{-1} due to $\nu(\text{C—CH}_3)$, ring

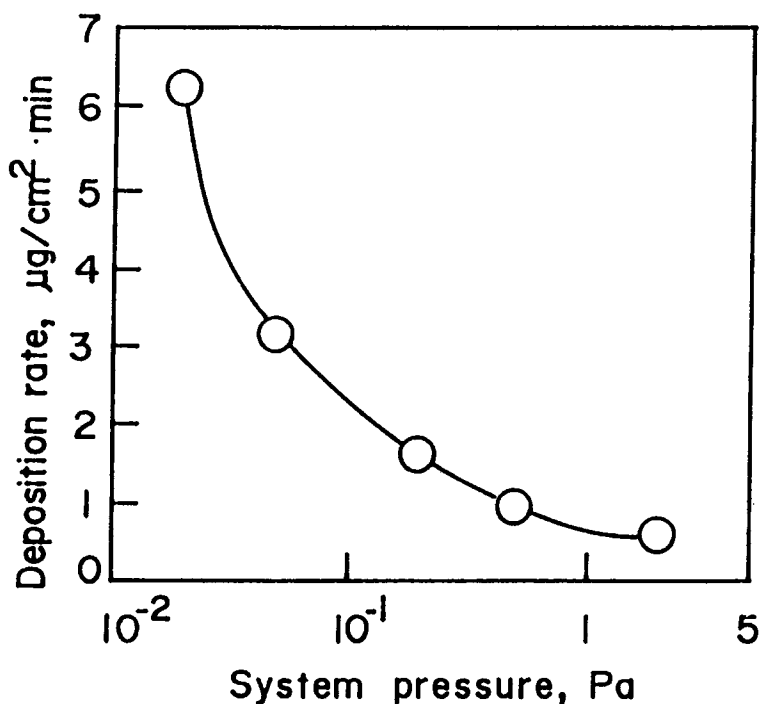


Fig. 2. Deposition rate of films prepared from aluminium-acetylacetonate complex at a RF power of 60 W as a function of the system pressure.

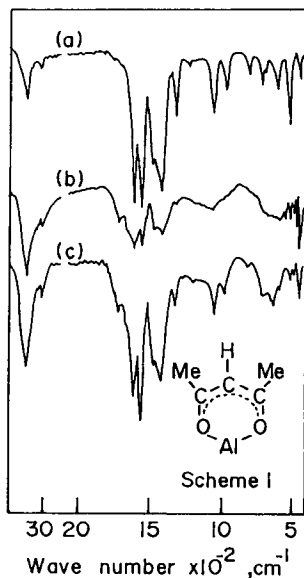


Fig. 3. IR spectra of films prepared from aluminium-acetylacetonate complex at a RF power of 60 W as a function of the system pressure: (a) monomer; (b) 2.6 Pa; (c) 6.6×10^{-2} Pa.

deformation, and $\nu(\text{Al}-\text{O})$; 770 cm^{-1} due to $\pi(\text{CH})$; 937 cm^{-1} due to $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{O})$, and $\delta(\text{C}-\text{O}-\text{C})$; 1025 cm^{-1} due to $\rho_r(\text{CH}_3)$; 1283 cm^{-1} due to $\nu(\text{C}-\text{CH}_3)$ and $\nu(\text{C}=\text{C})$; 1393 cm^{-1} due to $\delta(\text{CH}_3)$; 1463 cm^{-1} due to $\delta(\text{CH})$ and $\nu(\text{C}=\text{C})$; 1533 cm^{-1} due to $\nu(\text{C}=\text{O})$; 1594 cm^{-1} due to $\nu(\text{C}=\text{C})$. Among these absorptions the two absorption peaks at 1533 and 1594 cm^{-1} are characteristic of Al-AcAc complex.⁸

The plasma polymers deposited at a system pressure of 2.6 Pa (Fig. 3(b)) showed broad absorption peaks at 750 cm^{-1} due to $\pi(\text{CH})$; 937 cm^{-1} due to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$; 1022 cm^{-1} due to $\rho_r(\text{CH}_3)$; 1463 cm^{-1} due to $\nu(\text{C}-\text{CH}_3)$ and $\nu(\text{C}=\text{C})$; and at 1530 cm^{-1} and 1580 cm^{-1} which were characteristics of Al-AcAc complex. The absorption peaks related to Al-O and CH_3 groups (at 491 cm^{-1} , 579 cm^{-1} , 687 cm^{-1} , 1283 cm^{-1} , and 1393 cm^{-1}) disappeared. A new absorption peak at 1740 cm^{-1} due to carbonyl group appeared.

The plasma polymers prepared at a pressure of 2×10^{-2} Pa (Fig. 3(c)), on the other hand, showed similar spectra to those of Al-AcAc complex. The absorption peaks were sharper and more intense than the polymers prepared at 2.6 Pa. The sharp absorption peaks related to Al-O, $\text{C}-\text{CH}_3$, $\text{C}-\text{O}$ groups at 500 , 687 , 750 , 937 , 1022 , and 1287 cm^{-1} could be observed.

Comparison between the plasma polymers prepared at high and low system pressures suggests that the system pressure plays an important role in the formation of plasma polymers. The plasma polymerization at high pressure (several Pa) leads the scission of coordinating bonds of Al and AcAc moiety to yield aluminium oxide. The plasma polymerization at low system pressure (below 10^{-2} Pa) shows less bond scission. From these results we speculate that the increase of the system pressure leads to decrease the mean free path of sublimated molecules, and that as a result, accelerates the bond scission by enhanced collision.

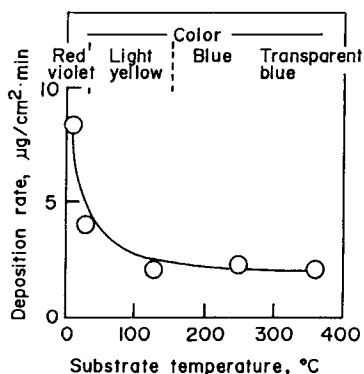


Fig. 4. The color and deposition rate of films prepared from aluminium-acetylaceton complex at a RF power of 60 W as a function of the substrate temperature.

Influences of the Substrate Temperature

The deposition rate of plasma polymers prepared at a pressure 6.6×10^{-2} Pa is shown in Figure 4 as a function of the substrate temperature. The deposition rate, as shown in Figure 4, decreased with increasing the substrate temperature. The polymer deposition rate was $8.7 \mu\text{g}/\text{cm}^2 \text{ min}$ at a substrate temperature of 10°C and was $2.2 \mu\text{g}/\text{cm}^2 \text{ min}$ at 360°C . This indicates that the substrate temperature also may be an important factor to control the formation of polymers. In addition to the polymer deposition rate, increasing of the substrate temperature led to the change of the color of the plasma polymers deposited. The color of plasma polymers changed from violet (at substrate temperatures of $10\text{--}15^\circ\text{C}$) to yellow (at substrate temperatures of $15\text{--}160^\circ\text{C}$) and blue (at substrate temperatures of $160\text{--}260^\circ\text{C}$). The color change may be related to the chemical composition of the plasma polymers.

The plasma polymers were analyzed by IR and XPS. Table I shows the Al/C, O/C, and O/Al atomic ratio (determined by XPS) of the plasma polymers as a function of the substrate temperature. The Al/C atomic ratio for the plasma polymers increased from 0.02 (at a substrate temperature of 25°C) to 0.23 (at 160°C) and to 0.32 (at 360°C). The O/C atomic ratio also increased from 0.46 (at 25°C) to 0.54 (at 160°C) and to 0.74 (at 360°C). The O/Al

TABLE I
The Al/C, O/C, and O/Al Atomic Ratio and Al-containing Residues of Plasma-Polymers^a

Substrate temperature (°C)	Al/C	O/C	O/Al	Al-content in polymer (%)
25	0.02	0.46	29.7	1.0
160	0.23	0.54	2.3	13.2
220	0.22	0.55	2.4	12.7
260	0.20	0.46	2.3	12.3
360	0.32	0.74	2.3	15.8

^a Prepared from aluminum-acetylaceton complex at a RF power of 60W as a function of the substrate temperature.

atomic ratio, when the substrate temperature raised from 25 to 160°C, decreased rapidly from 29.7 to 2.3, and afterward remained to be a constant of 2.3. This table indicates that the chemical composition of plasma polymers depends strongly on the substrate temperature. Polymers deposited on the substrate surface at low temperature (at 25°C) are rich in carbon moiety, and polymers deposited on the surface at high temperatures are rich in aluminium moiety. The color changes by the substrate temperature might result from the chemical composition of the plasma polymers.

Influences of the substrate temperature on chemical composition of the deposited polymers, furthermore, were investigated by means of IR spectroscopy (Fig. 5). The polymers deposited at a substrate temperature of 25°C (spectrum a) showed strong absorption peaks at 420 cm^{-1} and 690 cm^{-1} due to ring deformation of a coordinate bonding in Al—AcAc complex, at 1022 cm^{-1} due to $\rho_r(\text{CH}_3)$ and $\nu(\text{C—O})$, at 1463 cm^{-1} due to $\delta(\text{CH})$ and $\nu(\text{C=C})$, at 1530 cm^{-1} and 1590 cm^{-1} due to $\nu(\text{C=O})$ and $\nu(\text{C=C})$, at 2900 cm^{-1} due to $\nu(\text{CH}_3)$. When the substrate temperature increased to 160°C, the spectrum (b) was essentially similar to the former. However some absorption peaks at 780 cm^{-1} due to $\pi(\text{CH})$, at 1100 cm^{-1} due to C—H group, and at 1700 cm^{-1} due to carbonyl groups became intense. For the polymer deposited at a substrate temperature of 260°C (spectrum c), the absorption peaks at 720 cm^{-1} due to C=C and Al—O groups became remarkable intense. When the substrate temperature increased to 360°C the spectrum (d) showed that the absorption peaks at 1240 cm^{-1} due to C—O group as well as at 720 cm^{-1} due to C=C and Al—O became intense.

These spectral changes indicate that the high substrate temperatures (above 160°C) assist the decomposition reaction of Al—AcAc complex to yield polymers containing Al—O and C—O group.

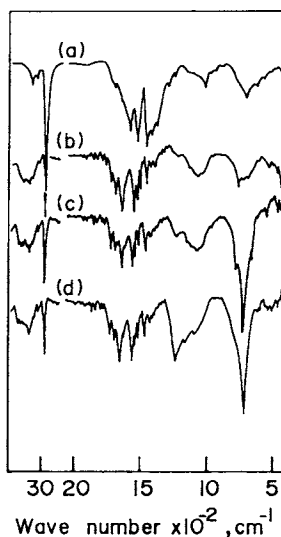


Fig. 5. IR spectra of films prepared from aluminium-acetylacetonate complex at a RF power of 60 W as a function of the substrate temperature: (a) R.T.; (b) 160°C; (c) 260°C; (d) 360°C.

Figure 6 shows typical C_{1s} and O_{1s} core level spectra for the plasma polymers deposited at substrate temperatures of 25, 220, and 360°C. The C_{1s} spectra were complex, and distributed widely in range of 282 to 292 eV. These C_{1s} spectra were deconvoluted into three or four C_{1s} components, which were assigned $C-C$ at 285.0 eV, $C-O$ at 286.0 eV, $C-C=O$ at 287.5 eV, and $O-C=O$ group at 289.6 eV. The C_{1s} spectrum of the polymer deposited at substrate temperature of 25°C showed three C_{1s} components ($C-C$ groups at 285.0 eV, $C-O$ groups at 286.4 eV, and $C=O$ groups at 288.1 eV). The plasma polymers deposited at 220 and 360°C showed four components ($C-C$, $C-O$, $C=O$, and $-O-C=O$ groups at 285.0, 286.4, 288.1, and 289.6 eV, respectively). The appearance of $-O-C=O$ groups at 289.6 eV, especially at 360°C, suggests the oxidation of carbon moieties.

The O_{1s} spectra were distributed from 528 to 539 eV. It is sure that the O_{1s} spectra involve more than two components of different binding energy, because of a wide FWHM value of 2.9 eV. However the spectra could not be deconvoluted because of monotonous curves. The O_{1s} spectrum for the plasma polymer prepared at 25°C was composed of a main peak at 531.3 eV with a shoulder at 529.6 eV. The O_{1s} peak at 531.3 eV was assigned Al-O groups.⁹ The O_{1s} spectra for the plasma polymers deposited at 220 and 360°C showed a peak at 532.2 eV without a shoulder at 529.6 eV due to C-O groups. These O_{1s} spectra indicate that a main oxygen residue of the plasma polymers deposited at 220 and 360°C may be Al-O groups. This assumption is supported from the Al_{2s} and Al_{2p} core level spectra.

Figure 7 shows Al_{2s} and Al_{2p} core level spectra for the plasma polymers at substrate temperatures of 25, 220, and 360°C. The polymers deposited at a substrate temperature of 25°C (spectrum a) showed weak and noisy Al_{2s} and Al_{2p} spectra because of low Al concentration. Accordingly, the Al_{2s} spectrum is not represented in Figure 7. The polymers deposited at 220 and 360°C showed intense and sharp Al_{2s} and Al_{2p} spectra. The Al_{2s} spectra at 220 and 360°C were consisted of a main peak at 119.5 eV. The Al_{2s} binding energy has been reported

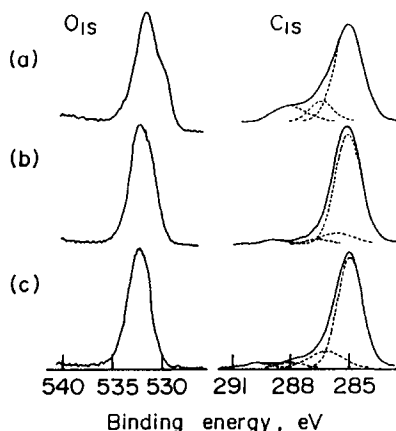


Fig. 6. ESCA (C_{1s} , O_{1s}) spectra of films prepared from aluminium-acetylacetonate complex at a system pressure of 6.6×10^{-2} Pa as a function of substrate temperature: (a) 25°C; (b) 220°C; (c) 360°C.

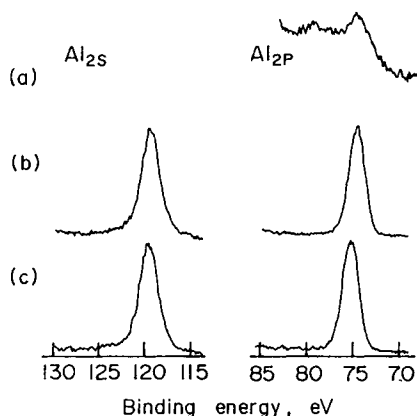


Fig. 7. ESCA (Al_{2s} , Al_{2p}) spectra of films prepared from aluminium-acetylaceton complex at a system pressure of 6.6×10^{-2} Pa as a function of substrate temperature: (a) 25°C; (b) 220°C; (c) 360°C.

to be 118 eV for Al metal and 128 eV for Al_2O_3 .⁹ Taking this report into consideration, it is guessed that Al atoms of the plasma polymers are oxides rather than metallic states. However either oxidation state of $\text{Al}-\text{O}-$, $\text{Al}(-\text{O}-)_2$, or $\text{Al}(-\text{O}-)_3$ is not clear.

These results indicate that the substrate temperature leads to changes in the chemical composition of the plasma polymers, especially carbon residues.

Influences of the RF Power

As mentioned above chapters we believe that the system pressure and the substrate temperature are important factors to control plasma polymerization reaction. It is well known that the RF power also is a major factor to control the plasma polymerization reactions.

Figure 8 shows the polymer deposition rate as a function of the RF power. When the RF power increased from 20 to 60 W, the deposition rate decreased from 14 to $6.4 \mu\text{g}/\text{cm}^2 \text{ min}$ at a system pressure of 2.6×10^{-2} Pa and from 5.8 to $3.6 \mu\text{g}/\text{cm}^2 \text{ min}$ at 6.6×10^{-2} Pa.

When the RF power increased from 20 to 60 W, the O/C atomic ratio increased from 0.22 to 0.46, and O/Al atomic ratio increased from 10 to 30. However the Al/C atomic ratio remained almost constant (0.02). The elemental composition of the plasma polymer also was changed by changing the RF power. The plasma polymers showed similar IR spectra independently of the RF power (Fig. 9). This indicates that polymers plasma-polymerized at different RF power (20–60 W) possess similar functional groups. From this sense, the RF power does not influence powerfully the polymer-forming reactions compared with powerful than that of the system pressure and the substrate temperature.

CONCLUSION

Influences of the system pressure and the substrate temperature on plasma polymerization reactions of aluminium-acetylaceton ($\text{Al}-\text{AcAc}$) complex were investigated by IR and XPS.

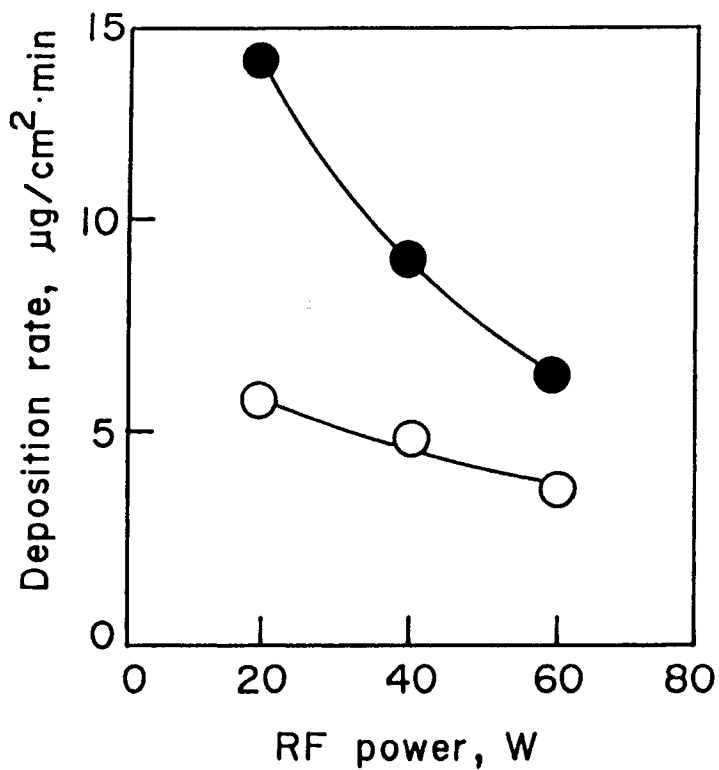


Fig. 8. Deposition rate of films prepared from aluminium-acetylacetonate complex as functions of the RF power and the system pressure: \circ at 6.6×10^{-2} Pa; \bullet at 2.6×10^{-2} Pa.

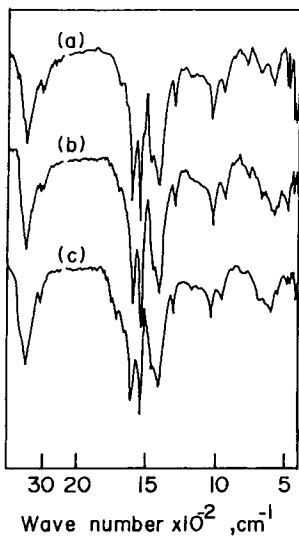


Fig. 9. IR spectra of films prepared from aluminium-acetylacetonate complex at a system pressure of 6.6×10^{-2} Pa as a function of RF power: (a) 20 W; (b) 40 W; (c) 60 W.

The system pressure and the substrate temperature play an important role in the formation of plasma polymers. The high system pressure and the high substrate temperature leads to the formation of plasma polymers rich in aluminium moieties. The low system pressure and the low substrate temperature leads to formation of plasma polymers rich in carbon moieties. Effects by the system pressure and the substrate temperature on the polymer-deposition process are more powerful than by the RF power.

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