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Influences of the substrate temperature on the films plasma-polymerized at the low system pressure

Junichi Ohkubo* and Norihiro Inagaki

Laboratory of Polymer Chemistry, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432 Japan

Summary

Influences of the substrate temperature and the system pressure on the plasma polymerization were investigated from a viewpoint of the chemical composition of the deposited polymers. Both parameters influenced the plasma polymerization of tetrafluoroethylene (TFE). The deposition at the high substrate temperature as well as at the low system pressure led to the formation of plasma polymers being poor in fluorine moieties. This result indicates that the chemical composition of the deposited plasma polymers may be determined by interactions of activated molecules with substrate surfaces.

Introduction

Plasma polymerization is a thin film process, where monomer molecules injected into plasma are fragmented by actions of plasma, especially electrons, the activated fragments are recombinated to grow larger molecules, and finally, polymers are formed by repitition of the fragmentation and the recombination. From the aspect of such polymer formation processes in plasma polymerizations, many investigators have been directed their attentions to what species are present in the plasma. The active species in plasma are mainly analyzed by MASS spectroscopy, ICP spectrometory, etc. Recently the development of diamond-like film formation by the plasma CVD technique emphasizes an importance of the substrate temperature. The importance of the substrate temperature can be pointed out also in the thin film-formation process by vacuum evaporation (VE) and molecular beam epitaxy (MBE). The film-formation by VE and MBE techniques involves three process, [1] the evaporation of low-molecules from the furnace, [2] the traveling of the evaporated molecules to the substrate, and [3] condensation process of the molecules on the substrate surface (1,2). The 2nd and the 3rd process are related to the system pressure and the substrate temperature. Actually, in plasma CVD of silicon compounds, the deposition rate and the chemical composition of the deposited polymers are depended on the substrate temperature (3-5). This concept may be realized also in the polymer-formation process by plasma polymerization although plasma polymerization involves chemical reactions in a gas phase (6). Yasuda et al. (7,8) proposed a parameter, sticking coefficient, which determines the polymer deposition. The sticking coefficient is defined as (number of molecules remaining on the substrate surface)/(number of total impinging molecules). Therefore, the

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*To whom offprint requests should be sent coefficient depends on kinetic energy of impinging molecules and also on the substrate temperature.

Taking these references into consideration, it is not unreasonable that the polymer deposition from plasma polymerization is controlled by the substrate temperature as well as the system pressure. In this study, plasma polymerization was carried out at a low pressure of 2.6×10^{-2} Pa to avoid collision of activated molecules in a gas phase. Influences of the substrate temperature on the plasma polymers were investigated by means of FT-IR spectroscopy and XPS. Tetrafluoroethylene (TFE) was used as a monomer for plasma polymerization.

Experimental

The apparatus used in this study for plasma polymerization was a capacitively-coupled system (13.56 MHz), which contained a parallel pair of electrodes, an electromagnetic coil, an inlet-tube for monomer gas, and a vacuum system (Figure 1) (9). The electromagnetic coil was used for maintaining a glow discharge at low system pressures less than 10^{-2} Pa.

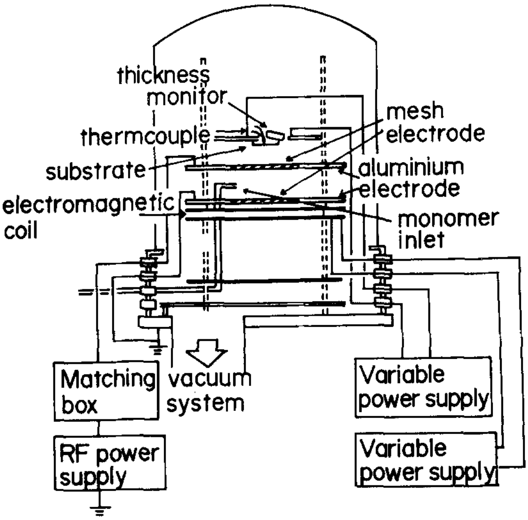

Figure 1 Schematic illustration of the HV apparatus equipped with plasma electrodes.

The surface of stainless sheets as a substrate was cleaned in organic solvents (trichloroethylene, acetone, and ethanol), then in the substrate-cleaning solution (Semico Clean 56) with an ultrasonic cleaner and, next, was cleaned by exposure of argon plasma. The reaction system was evacuated to less than 8×10^{-4} Pa, and TFE gas (adjused at 0.71 or 1.74 cm^3(STD)/min) was introduced into the reaction chamber. Plasma polymerizations were carried out under following conditions: the system pressure was 2.6 - 2.6×10^{-2} Pa, the RF power 60 W, the substrate temperature 25 - 220 °C, and the applied magnetic field 30 G.

IR spectra of the plasma polymers deposited on the stainless sheet were recorded by means of the ATR method with a JASCO fourier transform spectrometer FT/IR-3. XPS spectra were recorded with an ULVAC spectrometer 5400 (MgKα, 400 W). The complex C_{1s} spectra were subjected to the curve-fitting procedure using a nonlinear, least-square curve-fitting program provided by ULVAC.

Results and Discussion

Effects of the substrate temperature

Plasma polymerizations were performed at a RF power of 60 W and at a system pressure of 2.6×10^{-2} Pa, and polymers were deposited on the stainless sheet at temperatures from 25 °C to 220 °C. The elemental composition (the F/C atomic ratio) of the deposited plasma polymers, which was determined by XPS, was 1.20 (at a substrate temperature of 25 °C), 0.46 (at 160 °C), and 0.21 (at 220 °C). With increasing the substrate temperature the F/C atomic ratio of the deposited plasma polymers decreased. The elemental analysis indicates that the substrate temperature influences the composition of the deposited plasma polymers.

Figure 2 shows typical IR spectra of the deposited plasma polymers as a function of the substrate temperature. The plasma polymer deposited at 25 °C (spectrum a) showed strong absorption peaks at 680 cm^{-1} due to C=C, at 790 cm^{-1} due to C-F (bending vibration), at 1050 cm^{-1} due to CF_2 and CF (stretching vibration), at 1270 cm^{-1} due to CF_3 (stretching vibration), and at 1570, 1660 and 1730 cm^{-1} due to C=C and C=O groups. The plasma polymer deposited at 160 °C (spectrum b) showed that sharp absorption peaks appeared at 540 cm^{-1} due to O_2F radical (10,11), at 700 cm^{-1} due to C=C, and at 1500 - 1800 cm^{-1} due to C=C and C=O groups; and that the absorption peaks related to C-F groups (at 790, 1050, and 1270 cm^{-1}) became weak compared with those for the plasma polymers deposited at 25 °C (spectrum a). The plasma polymer deposited at 220 °C (spectrum c) showed essentially same as the spectrum (b).

These changes in infrared spectra indicate that the deposited plasma polymers are fluoro-polymers

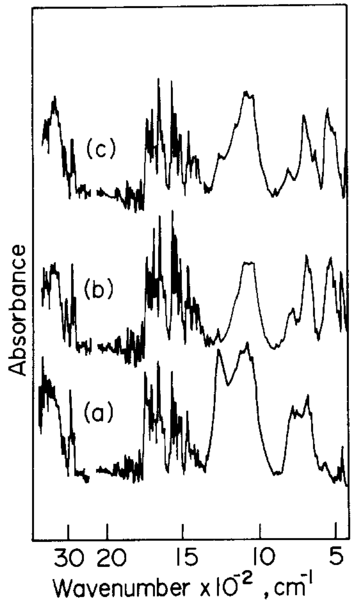

Figure 2 IR spectra for plasma polymers of TFE as a function of the substrate temperature: (a); 25 °C, (b);160 °C, (c);220 °C.

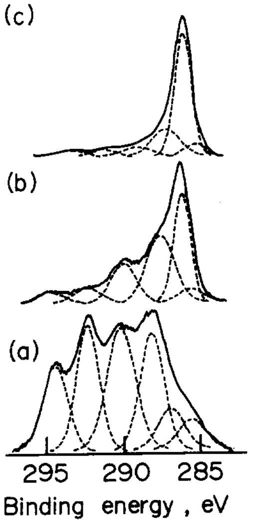

Figure 3 ESCA(C_{1s}) spectra for plasma polymers of TFE as a function of the substrate temperature: (a);25 °C, (b);160 °C, (c);220 °C.

containing C=C and C=O groups, and that the deposition at high temperatures leads to the formation of plasma polymers poor in highly-fluorinated carbon units (CF_3, CF_2 groups).

Furthermore the details of the deposited plasma polymers were investigated by XPS. Figure 3 shows the C_{1s} core level spectra for the plasma polymers at various substrate temperatures of 25, 160, and 220 °C. The C_{1s} spectrum for the plasma polymer prepared at 25 °C (spectrum a) distributed in range of 283 - 298 eV. When the substrate temperature increased from 25 to 160 and 220 °C, the C_{1s} spectra distributed narrowly at 280 - 294 eV (at 160 °C) and at 280 - 293 eV (at 220°C). The C_{1s} spectra were complex, and deconvoluted into five or six C_{1s} components. Clark et al. (12) reported that the chemical shifts in C_{1s} binding energy were 2.9 and 0.7 eV for the primary and secondary effects of replacing hydrogen, respectively. The C_{1s} component appearing at 285.0 - 287.8 eV (component I) was assigned to hydrocarbon-like carbon in environments with fluorine. The component from 287.9 to 290.7 eV (component II) was assigned to CHF groups, that from 290.8 to 293.6 eV (component III) to CF_2 groups, and that from 293.7 to 295.1 eV (component IV) was assigned to CF_3 groups. The component II involves the contribution of C=O groups. The relative area of each deconvoluted peak is listed in Table 1. When the substrate temperature increased from 25 to 160 and 220 °C, the component IV (due to CF_3 groups) decreased from 16.2 to 5.1 and 3.5 %, respectively. The component III (due to CF_2 groups) also decreased from 21.7 (at 25 °C) to 7.2 (at 160 °C) and 3.8 % (at 220 °C). On the contrary the component I increased remarkably from 14.4 to 38.1 or 64.7 % with increasing the substrate temperature.

From these results we conclude that the substrate temperature surely determines the chemical composition of plasma polymers. This may be explained from an aspect that less-fluorinated molecules rather than highly-fluorinated molecules are easy to be condensed on the substrate surface at high temperature.

Table 1 The relative area of C_{1s} component of plasma polymers prepared from TFE as functions of the substrate temperature and the system pressure.

substrate temperature(°C)	system pressure(Pa)	C_{1s} component (relative peak area in %)			
		I	II	III	IV
25	2.6×10^{-2}	14.4	47.7	21.7	16.2
160	2.6×10^{-2}	38.1	49.6	7.2	5.1
220	2.6×10^{-2}	64.7	28.0	3.8	3.5
25	2.6×10^{-2}	14.4	47.7	21.7	16.2
25	2.6×10^{-1}	11.0	53.3	20.1	15.6
25	2.6	7.4	55.2	21.7	15.7

The component I, II, III, and IV mean hydrocarbon-like, CHF, CF_2, and CF_3 groups, respectively.

Effects of the system pressure

Plasma polymerizations were performed as a function of the system pressure to investigate how the system pressure influenced on the plasma polymerization reactions. The formed plasma polymers were deposited at a substrate temperature of 25 °C. The elemental composition (the F/C atomic ratio) of the deposited polymers was a constant (1.20 - 1.14) independently of the system pressure. Figure 4 shows IR spectra of plasma polymers as a function of the system pressure. The plasma polymer prepared at a system pressure of 2.6×10^{-2} Pa (spectrum a) showed absorption peaks at 790 (C-F bending vibration), 1050 (C-F stretching vibration in CF_2 and CF groups) and 1270 cm^{-1} (C-F stretching vibration in CF_3 groups), at 680 and 1660 cm^{-1} due to C=C groups, and at 1730 cm^{-1} due to C=O group. When the system pressure increased to 2.6×10^{-1} (spectrum b) and 2.6 Pa (spectrum c), strong absorption peaks appeared at 745 and 1230 cm^{-1} due to C-F groups, and at 1570, 1660, and 1730 cm^{-1} due to C=C and C=O groups. The absorption peak at 1050 cm^{-1} was weak intensity compared with the spectrum (a).

Figure 5 shows the C_{1s} core level spectra for plasma polymers prepared as a function of the system pressure. All the C_{1s} spectra were deconvoluted into six C_{1s} components. Table 1 shows the relative area of each deconvoluted peaks of XPS spectra. When the system pressure increased from 2.6×10^{-2} Pa to 2.6 Pa, a relative peak area of the component I decreased from 14.4 to 7.4 %, and that of the component II increased from 47.7 to 55.2 %.

These results indicate that the system pressure influences on the chemical composition of the plasma polymers to be deposited,

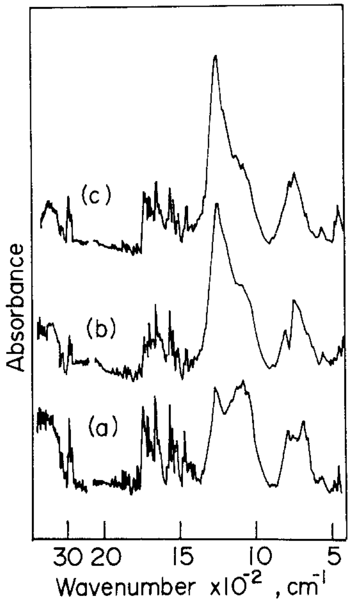

Figure 4 IR spectra for plasma polymers of TFE as a function of the system pressure: (a);2.6×10^{-2} Pa, (b);2.6×10^{-1} Pa, (c);2.6 Pa.

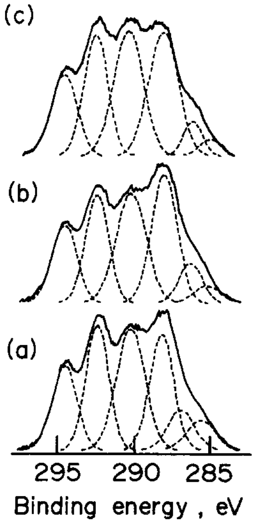

Figure 5 ESCA(C_{1s}) spectra for plasma polymers of TFE as a function of the system pressure: (a);2.6×10^{-2} Pa, (b);2.6×10^{-1} Pa, (c);2.6 Pa.

for instance less deposition of hydrocarbon-like carbons at high system pressure.

Conclusions

Influences of the substrate temperature and the system pressure on the plasma polymerizations of tetrafluoroethylene (TFE) were investigated by IR and XPS.

The substrate temperature strongly influences the chemical composition of the plasma polymers. High substrate temperatures lead to the deposition of the plasma polymers poor in fluorine moieties. The substrate temperature, which is as a factor of the plasma polymer formation, influences the chemical composition of the plasma polymers more than the system pressure.

References

1. Japan society for the promotion of science 131st committee (thin film), "Thin film handbook", Ohmsha, Tokyo(1983).
2. B. Pamplin, "Molecular beam epitaxy", Pergamon, Oxford(1980).
3. A. Wrobel, J. Klemberg, M. Wertheimer, and H. Schreiber, J. Macromol. Sci. Chem., A15, 197(1981).
4. D. Secrist and J. Mackenzie, J. Electrochem. Soc., 113, 914(1966).
5. J. Knights, Jpn. J. Appl. Phys., 18, 101(1979).
6. H. Yasuda and C. Wang, J. Polym. Sci., Polym. Chem. Ed., 23, 87(1985).
7. M. Gazicki, G. Surendran, W. James, and H. Yasuda, J. Polym. Sci., Polym. Chem. Ed., 23, 2255(1986).
8. M. Gazicki, G. Surendran, W. James, and H. Yasuda, J. Polym. Sci., Polym. Chem. Ed., 24, 215(1986).
9. J. Ohkubo and N. Inagaki, Shinkuu, 31, 960(1988).
10. R. Spratley, J. Turner, and G. Pimentel, J. Chem. Phys., 44, 2063(1966).
11. A. Arkell, J. Am. Chem. Soc., 87, 4057(1965).
12. D. T. Clark and W. Feast, J. Macromol. Sci., Revs. Macromol. Chem., 12, 191(1975).

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