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Preparation of thin films containing sulfonic acid and carboxylic acid groups by plasma polymerization of perfluorobenzene/sulfur dioxide and perfluorobenzene/carbon dioxide mixtures

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SUMMARY

Plasma polymerizations of the mixture of perfluorobenzene (PFB) and sulfur dioxide (SO_2) or carbon dioxide (CO_2), and the mixture of benzene (BZ) and SO_2 or CO_2 were investigated to obtain plasma polymer films with ionic groups such as sulfonic or carboxylic acid groups. The plasma polymerization of the mixture of PFB or BZ and SO_2 gave plasma polymer films containing sulfonic acid groups. The plasma polymerization of the mixture of PFB and CO_2 deposited plasma polymer films with carboxylic acid groups but that of the BZ/CO_2 mixture deposited plasma films with no carboxylic acid groups.

INTRODUCTION

Plasma polymerization is a thin-film-forming process. Monomer molecules introduced into plasma are activated and fragmented by the actions of plasma, and finally polymers deposit frequently in a thin-film form [1]. Therefore the chemical composition of the deposited polymers is difficult to predict beforehand from the monomer used for the plasma polymerization. The chemical composition of the plasma polymers is mainly depended on how monomer molecules are fragmented by the actions of plasma. The plasma polymerization technique is an unreliable process from the viewpoint of the molecular design but is of interest in a capability that polymers with unexpected chemical composition could be formed.

Polymers containing ionic groups such as sulfonic and carboxylic acids are interesting in electrical, ion exchange, and biocompatible properties. Many investigators [2-4] tried the preparation of polymer films containing ionic groups by plasma polymerization, but the trials did not succeed satisfactorily because of easy elimination of sulfur and oxygen atoms in a discharge state. The plasma of the mixture of fluorocarbons and oxygen shows strong oxidative ability and the ability is used for the etching process of photoresist and silicon in semiconductor industry [5]. This study aims to obtain thin films containing sulfonic or carboxylic acid groups by plasma polymerization. Plasma polymerizations of the mixture of per-fluorobenzen and sulfur dioxide or carbon dioxide are investigated and also are compared with the plasma polymerizations of the mixture of benzene and sulfur dioxide or carbondioxide.

EXPERIMENTAL

Plasma Polymerization

The reaction chamber used in this study for the plasma polymerization was an inductively coupled system operating at a frequency of 13.56 MHz (rf). It consisted of a Pyrex glass tube (100 mm inner diameter and 400 mm long) with a monomer inlet, a pressure gauge, a vacuum system of the combination of a rotary and a diffusion pump, a matching network for the inductive coupling of the rf power source, and a substrate stage for the plasma polymer deposition, which was positioned horizontally in the glass tube reactor. The details of the reaction chamber have been given in the literature [6].

The experimental procedures for the plasma polymerization were essentially the same as reported elsewhere [6]. The reaction chamber was evacuated to approximately 0.13 Pa,

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*To whom offprint requests should be sent and the surface of substrates (glass plates and silicon wafers) for the plasma polymer deposition was exposed to argon plasma, operated at an argon flow of 7 cm^3(STP)/min, at 1.3 Pa, and at a rf power of 50 W for 10 min, in order to eliminate water adsorbed on the substrate surface. The reaction chamber was once again evacuated to 0.13 Pa, and then monomer gas adjusted to a flow rate of 4 cm^3(STP)/min at 1.3 Pa, was introduced into the reaction chamber. The plasma polymerization was continued at a rf power of 100 W for 0.5 - 1.0 h.

Perfluorobenzene (PFB) (purchased from Fluorochem Ltd., U.S.A., more than 97 % purity), benzene (BZ) (purchased from Tokyo Kasei Kogyo Co., Japan, analytical grade), sulfur dioxide (SO_2), and carbon dioxide (CO_2) (purchased from Takachiho Tradeing Co., Japan, 99.9% purity) were used as monomers. Prior to the plasma polymerization PFB and BZ stored in the glass reservoir were degassed three times by evaporation under liquid nitrogen cooling.

Infrared Spectra and X-Ray Photoelectron Spectra

Plasma polymers deposited on the glass plate and scraped from the plate were used as specimens, and KBr disks were molded from the mixture of the plasma polymer specimens and KBr powder. IR spectra of the disks were recorded on a Nihon Bunko Fourier transform spectrometer FT/IR-3.

Plasma polymer films (approximately 100 nm thick) deposited on silicon wafers were used for the measurement of XPS spectra. XPS spectra of the polymer films were recorded on an Ulvac-Phi electronspectrometer 5300 using Mg K_α photon source (a voltage of 15 kV, a wattage of 400 W, and a background pressure of 1.3 x 10^{-5} Pa). The following sensitivity factors (S) for the core levels were used to calculate the relative atomic concentration of the plasma polymers: $S(C_{1s}) = 1.00$, $S(O_{1s}) = 2.64$, $S(F_{1s}) = 4.00$, and $S(S_{2p}) = 2.16$.

RESULTS AND DISCUSSION

The plasma polymerization of the PFB/SO_2, PFB/CO_2, BZ/SO_2, and BZ/CO_2 mixture deposited films. The films changed their color from light-yellow to dark brown depending on the SO_2 or CO_2 concentration. Table 1 shows the polymer deposition rate in the plasma polymerization of the PFB/SO_2, PFB/CO_2, BZ/SO_2, and BZ/CO_2 mixtures as a function of the SO_2 or CO_2 concentration. The polymer deposition rate, as shown in Table 1, decreases with increasing the SO_2 or CO_2 concentration. At SO_2 and CO_2 concentrations of over 50 mol% the deposition rate except in the plasma polymerization of the BZ/CO_2 mixture becomes 2 - 4 times less, and at SO_2 and CO_2 concentrations more than 80 mol%, finally, no polymer deposits.

Table 1 Polymer Deposition Rate in the Plasma Polymerization of the PFB/SO_2, PFB/CO_2, BZ/SO_2, and BZ/CO_2 Mixtures

SO_2 or CO_2 Concentration (mol%)	Polymer Deposition Rate (mg/cm^2-h)			
	PFB/SO_2 Mixture	BZ/SO_2 Mixture	PFB/CO_2 Mixture	BZ/CO_2 Mixture
0	888	804	888	804
14.3	-	-	846	798
25	978	774	798	-
50	217	458	-	762
60	-	-	466	-
75	17.0	9.4	76.8	636
80	~0	~0	~0	50.2

The plasma polymers deposited from the PFB/SO_2 mixtures contained C, F, O, and S atoms; and the plasma polymers from the PFB/CO_2 mixtures also contained C, F, and O atoms. The polymers plasma-polymerized from the BZ/SO_2 mixtures involved C, O, and S atoms; and the polymers from the BZ/CO_2 mixtures involved C and O atoms. Table 2 shows a typical elemental composition of the plasma polymers as a function of the SO_2 or CO_2 concentration. When the SO_2 or CO_2 concentration is restricted to less than 50 mol% the SO_2 or CO_2 addition gives less effect on the elemental composition of the plasma polymers deposited from the PFB/SO_2 and PFB/CO_2 mixtures. The F/C atomic ratio for the plasma polymers is 0.86 (0 mol%SO_2), 0.86 (50 mol%SO_2), and 0.77 (50 mol%CO_2); and the O/C atomic ratio is 0.11 (0 mol%SO_2), 0.14 (50 mol%SO_2), and 0.12 (50 mol%CO_2). However, when the SO_2 or CO_2 concentration is 75 mol%, the SO_2 or CO_2 addition gives large changes in the elemental composition of the plasma polymers. The F/C atomic ratio decreases largely from 0.86 to 0.29 (75 mol%SO_2) and 0.27 (75 mole%CO_2) (3 times less), and the O/C atomic ratio increases from 0.11 to 1.16 (75 mol%SO_2) and 1.42 (75 mol%CO_2) (12 times larger). The S/C atomic ratio for the plasma polymers deposited from the PFB/SO_2 mixtures is changeless value of 0.11 - 0.18 independently of the SO_2 concentration. Similar effects of the SO_2 and CO_2 addition are observed in the plasma polymerization of the BZ/SO_2 and BZ/CO_2 mixtures containing a high SO_2 or CO_2 concentration of 75 mol%.

Table 2 Elemental Composition of the Plasma Polymers deposited from the PFB/SO_2, PFB/CO_2, BZ/SO_2, and BZ/CO_2 Mixtures

Mixture	SO_2 or CO_2 Concentration (mol%)	Relative Atomic Ratio		
		F/C	O/C	S/C
PFB/SO_2	0	0.86	0.11	0
	50	0.86	0.14	0.11
	75	0.29	1.16	0.18
BZ/SO_2	0	0	0.12	0
	50	0	0.31	0.20
	75	0	0.34	0.26
PFB/CO_2	0	0.86	0.11	0
	50	0.77	0.12	0
	75	0.27	1.42	0
BZ/CO_2	0	0	0.12	0
	50	0	0.18	0
	75	0	0.23	0

From these results we conclude that (1) SO_2 molecules in a plasma interact with PFB and BZ molecules to form plasma polymers containing much amount of oxygen and sulfur atoms. CO_2 molecules also interact with PFB and BZ molecules to form plasma polymers containing much amount of oxygen atoms, (2) in addition to the oxygen and sulfur incorporation defluorination reactions from PFB molecules occur in the plasma polymerization of the PFB/SO_2 and PFB/CO_2, and (3) the interactions of SO_2 and CO_2 molecules in plasma with PFB or BZ molecules occur predominantly at the SO_2 and CO_2 concentrations of more than 75 mol%.

Fig. 1 and 2 show typical IR spectra of the plasma polymers formed from the PFB/SO_2 and BZ/SO_2 mixtures containing a SO_2 concentration of 75 mol% . The plasma polymers show characteristic absorption peaks at 1380 and 1230 cm^{-1} due to asymmetric and symmetric stretching vibration of SO_2 in R-O-SO_2-O-R' (sulfate) and at 1170 and 1050 cm^{-1} due to asymmetric and symmetric stretching vibration of SO_2 in R-SO_2OH (sulfonic acid) [7]. And the plasma polymers formed from the PFB/SO_2 mixture also show characteristic absorption peaks related to fluorine moieties at 1735 cm^{-1} due to the stretching vibration of C=O and C=C in -CF=CF- groups and at 1230 cm^{-1} due to the stretching vibration of C-F groups (Fig. 1). These spectra indicate the possibility that sulfonic acid and sulfate groups may be formed from the plasma polymerization of the PFB/SO_2 and BZ/SO_2 mixtures. The presence of sulfonic acid groups in the plasma polymers is supported by the XPS spectra. The S_{2p} core level spectra involved two peaks at 164.1 and 169.0 eV for the plasma polymers formed from the PFB/SO_2 mixture; and at 164.2 and 168.7 eV for the plasma polymers from the BZ/CO_2 mixture. This indicates that there are at least two different sulfur moieties whose the sulfur atoms are different in electonic state. The binding energy of S_{2p} core level mainly depends on the oxidation state of sulfur atoms: the binding energy is 163.9 eV for $\underline{S}$-C, 165.2 eV for $\underline{S}$-O, 166.0 eV for $\underline{S}$(O), 167.5 eV for $\underline{S}O_2$, 168.3 eV for $\underline{S}O_3$, and 169.4 eV for $\underline{S}O_4$ [8]. This reference shows that the plasma polymers plasma-polymerized from the PFB/SO_2 and BZ/SO_2 mixtures contain highly oxidized sulfur atoms (SO_3 and SO_4) and low oxidized sulfur atoms (S-C).

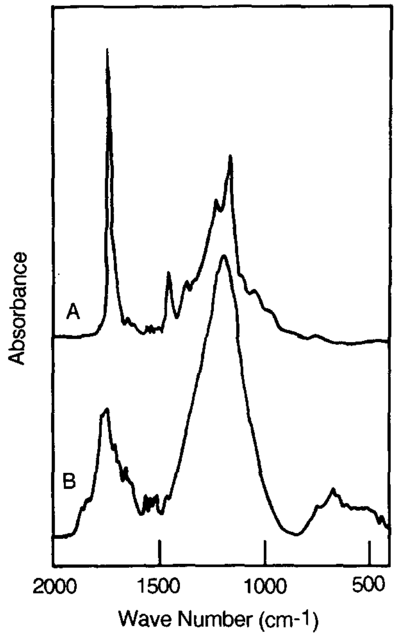

Fig. 1 IR Spectra of Plasma Polymers prepared from PFB/SO_2 (75 mol% SO_2) (A) and PFB/CO_2 Mixtures (75 mol% CO_2) (B).

Fig. 2 IR Spectra of Plasma Polymers prepared from BZ/SO_2 (75 mol% SO_2) (A) and BZ/CO_2 Mixtures (75 mol% CO_2) (B).

Fig. 1 and 2 show typical IR spectra of the plasma polymers formed from the PFB/CO_2 and BZ/CO_2 mixtures containing a CO_2 concentration of 75 mol%. The plasma polymer from the PFB/CO_2 mixture show strong and broad absorption peaks at 1700 - 1750 cm^{-1} due to the stretching vibration of C=O in C(O)OH and C(O)OR groups, at 1700 and

1650 cm^{-1} due to C=O stretching vibration in ketons and -C(O)-C=C groups, respectively [7]. The plasma polymers from the BZ/CO_2 mixture show strong absorption peaks at 1650 cm^{-1} due to unsaturated carbonyl groups [7]. The comparison in the IR spectra points out that the presence of C(O)OH and C(O)OR groups whose the C=O stretching vibration appears at higher wave number (1700 - 1750 cm^{-1}) distinguishes the polymers films plasma-polymerized from the PFB/CO_2 mixture from those plasma-polymerized from the BZ/CO_2 mixture. This presence of C(O)OH and C(O)OR groups is supported by the XPS spectra. The plasma polymers formed from the PFB/CO_2 mixture showed five C_{1s} components at 285.0 ($\underline{C}H$), 287.8 ($\underline{C}F$), 289.5 ($\underline{C}(O)O$ and $\underline{C}F$-CF_n), 291.8 ($\underline{C}F_2$), and 293.3 eV ($\underline{C}F_3$) [9]. While, the plasma polymers formed from the BZ/CO_2 mixture shows three C_{1s} components at 285.0 ($\underline{C}H$), 286.5 ($\underline{C}$-O), and 288.0 eV ($\underline{C}$=O) [10]. And the treatment of the plasma polymers prepared from the PFB/CO_2 mixture with ammonia gas brought about the appearance of a new absorption peak at 1395 cm^{-1} due to NH_4^+ groups [9]. This indicates surely the presence of acidic groups in the plasma polymers.

In conclusion, the plasma polymerization of the PFB/SO_2 and BZ/SO_2 mixtures, which contain a SO_2 concentration of 75 mol%, yields thin films containing ionic SO_3H groups. The plasma polymerization of the PFB/CO_2 mixture containing 75 mol% CO_2 yield thin films containing ionic C(O)OH groups, but that of the BZ/CO_2 mixture do not formation C(O)OH-containing plasma films. The success in the formation of SO_3H and C(O)OH groups by the plasma polymerization of PFB/SO_2 and PFB/CO_2 mixtures may be due to assistance of strong oxidative species generated from the plasma of PFB/SO_2 mixture. The oxidative species generated from the plasma of PFB/SO_2 mixture will be analyzed and discussed in a next paper.

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