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The study of plasma stability of poly(organophosphazene) films prepared on silicon wafers

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Six poly(organophosphazenes) were prepared by the reaction between polydichlorophosphazene and alkoxides, phenoxides or amine compounds. The plasma stability of their films prepared on silicon wafers was investigated with an ellipsometer and ESCA; the plasma used was poly(bisanilinophosphazene) and the stability was similar to novolak resin.

1. Introduction

Poly(organophosphazenes) $(NPR_2)_n$ prepared from polydichlorophosphazene $(NPCl_2)_n$ and the various nucleophilic reagents such as alkoxides, phenoxides and amines had varied chemical and physical properties. For example, some poly(organophosphazene) membranes had the function of gas separation under dry or wet conditions as described by Kajiwara [1, 2]. Special elastomers for O-rings, lip-seals, arctic fuel hoses, gaskets, vibration damping equipment and coated fabrics have also been developed by the Firestone Tire and Rubber company [3]. Furthermore, biocompatibility testing of some poly(organophosphazenes) has shown them to be as compatible with rat muscle tissue as Silasic silicon rubber [4], and poly(bismethylaminophosphazene) has been used as a carrier molecule for anticancer drugs [5–7]. Poly(organophosphazenes) have also been known to resist oxidative break down and have provided good uniform films for lithographic application [6, 7]. Recently, with increased application of multilayer lithographic processes, poly(organophosphazenes) may be found to be interesting lithographic materials like poly(siloxanes) [8] and poly(silanes) [9], since they have high oxygen resistance. This paper investigates the plasma stability of some poly(organophosphazene) films.

2. Experimental procedure

2.1. Preparation of hexachlorocyclotriphosphazene $(NPCl_2)_3$ and polydichlorophosphazene $(NPCl_2)_n$

$(NPCl_2)_3$ was prepared from the reaction with 500 g of phosphorus pentachloride (PCl_5) and 200 g of ammonium chloride (NH_4Cl) using 1500 ml of tetrachloroethane or chlorobenzene [10]. Pure $(NPCl_2)_3$ (m.p. 112 °C) was obtained by repeated vacuum distillation.

Linear polydichlorophosphazene $(NPCl_2)_n$ was prepared by the method of Kajiwara [11], that is, 20 to 30 g of $(NPCl_2)_3$ and 0.1 to 0.2 g of sulphur recrystallized from benzene were placed in a pyrex tube which was evacuated to 10 torr for 1 h. Dry nitrogen was then introduced at atmospheric pressure, the sealed tube was placed in an electric furnace at 280–300 °C for 0.5 to 1.0 h. After the polymerization was complete, the polymer and oligomer mixture was dissolved in 1 l of dry terehydrofuran (THF). To remove the oligomer, the THF solution was added to n-heptane. After $(NPCl_2)_n$ precipitated, the precipitate was separated by decantation, followed by dissolution in THF and precipitation. This purification procedure was repeated several times and the purified $(NPCl_2)_n$ was then dissolved in THF.

2.2. Preparation of poly(organophosphazenes) $(NPR_2)_n$

2.2.1. $[NP(OCH_2CF_3)_2]_n$

A solution of sodium trifluoroethoxide was prepared by addition of sodium 2,2,2-trifluoroethanol in dry THF. The reaction was exothermic and the mixture was heated to keep the solvent boiling for 20 h. At the conclusion of the reaction, the mixture was cooled and acidified with dilute hydrochloric acid, and benzene was added to coagulate the polymer. After isolation of the polymer by filtration, it was washed with a large excess of water to remove salts and then precipitated from THF into benzene to remove oligomer and low-molecular-weight polymers. The polymer was then exhaustively dried under vacuum.

2.2.2. $[NP(OCH_2CH_3)_2]_n$

A solution of $(NPCl_2)_n$ in benzene was added slowly to a stirred solution of sodium ethoxide prepared from sodium and ethanol in a nitrogen atmosphere. The

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reaction was allowed to proceed at 25 °C for 5 days. The mixture was added to distilled water and the polymer precipitated was isolated by filtration. Furthermore, purification of the polymer was carried out in THF-ethanol.

2.2.3. $[NP(NHC_6H_5)_2]_n$ and $[NP(NHC_6H_4Cl\text{-}p)_2]_n$

A solution of $(NPCl_2)_n$ in THF was added to a solution of aniline in THF and triethylamine mixture solvent. The mixture was boiled for 48 h and then kept at 25 °C for 1 week. The reaction mixture was added into distilled water, and the polymer precipitated was dissolved in THF solvent. Furthermore, the purification of polymer was carried out with the method of reprecipitation. $[NP(NHC_6H_4Cl\text{-}p)_2]_n$ was also prepared in a similar way to $[NP(NHC_6H_5)_2]_n$.

2.2.4. $[NP(OC_6H_5)_2]_n$ and $[NP(OC_6H_4Cl\text{-}p)_2]_n$

A solution of $(NPCl_2)_n$ in THF was added slowly to a stirred solution of sodium phenoxide prepared from sodium and phenol in THF. After the mixture was refluxed at 74 °C for 24 h, THF solvent was then added to n-heptane. The precipitations were filtered off, washed with acetone and dried under the vacuum condition overnight. $[NP(OC_6H_4Cl\text{-}p)_2]_n$ was prepared in a similar way to $[NP(OC_6H_5)_2]_n$.

2.3. Preparation of films of poly(organophosphazene) on silicon wafer

The solution of 10 wt % of the polymer was prepared to form the films on silicon wafer having the dimension of 2″ × 2″ (inch) × 300 μm, that is, $[NP(OC_6H_5)_2]_n$ and $[NP(OCH_2CH_3)_2]_n$ were dissolved in DMF, $[NP(NHC_6H_5)_2]_n$ and $[NP(HNC_6H_4Cl\text{-}p)_2]_n$ in 2-methoxyethyl acetate, $[NP(OC_6H_4Cl\text{-}p)_2]_n$ or $[NP(OCH_2CF_3)_2]_n$ in monochlorobenzene or methylisobutylketone. After they were spun on silicon wafer, the wafer was heated on a hot plate at 100 °C for 1 h. The thickness of the films prepared on silicon wafer were also determined with an ellipsometer made by Yokojiri Kogaku Co., Ltd.

2.4. The measurement of the stability of poly(organophosphazene) for plasma (CF_4–O_2)

The stability of poly(organophosphazene) films for plasma was evaluated with the change of thickness of the films. The pressure used was 1, 5 and 20 Pa and etching time was 1 or 2 min under 0.08 W cm^{-2} of power density.

2.5. Instrument

The ion etching machine was a parallel plate type reactive from DEM 451 Aneruba Co., Ltd and the ESCA was an XSAM-800 from Kratos Co., Ltd.

3. Results and discussion

3.1. Reactive ion etching rate (RIE)

Refractive indices of poly(organophosphazene) films calculated from the ellipsometer are summarized in Table I. It is found from Table I that the index of the film with aromatic side chains is higher than that with aliphatic side chains. The RIE of poly(organophosphazene) films spin coated onto silicon wafer were also measured under 5 Pa, 0.08 W cm^{-2} using plasma (CF_4 sccm, O_2 sccm). Table I also shows the relation between the decreased film thickness and time which was investigated with an ellipsometer. It is found that poly(organophosphazene) films having aliphatic side chains such as ethoxy or trifluoroethoxy do not have as good RIE as novolak resin (LMR). $[NP(OCH_2CH_3)_2]_n$ has a lower RIE than that of $[NP(OCH_2CH_3)_2]_n$. Poly(organo-phosphazene) films with aromatic side chains such as phenoxy aniline also have a lower RIE than those with side chains such as p-chlorophenoxy and p-chloroaniline. Furthermore, the RIE of $[NP(OC_6H_5)_2]_n$ and $[NP(HNC_6H_5)_2]_n$ are better than that of LMR. The time the films disappeared completely from silicon wafer surface is then estimated with the use of Table I. Typical results are given in Fig. 1.

It is found from Fig. 1 that the RIE depends on the time. The straight lines given in Fig. 1 are extrapolated to find the final time and the results are summarized in Table I. From Table I it is indicated that the film of poly(bisanilinophosphazene) has the lowest RIE as well as LMR. The films of poly(organophosphazenes) having aromatic amines have a good RIE in comparison with others.

3.2. Reactive ion etching rate (RIE) under various pressures

The RIE of the films is investigated with an ellipsometer under various pressures and the film thicknesses which disappeared are summarized in Table II. It is found from Table II that the rate of disappearance of poly(bistrifluoroethoxyphosphazene) film increased with increasing pressure. Consequently, poly(bistrifluoroethoxyphosphazene) film has no resistance for plasma. On the other hand, the rate of the disappearance of films having aromatic side chains decreased with increasing pressure except for poly(bisanilinophosphazene) film which reached a steady state when the pressure was greater than 5 Pa. This means that poly(bisanilinophosphazene) film has resistance for plasma under higher pressure.

3.3. ESCA study of poly(organophosphazene) film without and with plasma

Poly(organophosphazene) films such as $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2CH_3)_2]_n$, $[NP(HNC_6H_5)_2]_n$ and $[NP(NHC_6H_4Cl\text{-}p)_2]_n$ prepared without (A) and with (B) plasma on a silicon wafer is investigated by ESCA and the spectra are given in Figs 2 to 5. The maximum peak of F_{1s}, O_{1s},

TABLE I Refractive index and RIE of poly(organophosphazene) films prepared on silicon wafer under 5 Pa using the plasma (CF_4 40 sccm, O_2 4 sccm, 0.08 $W cm^{-2}$)

$(NPR_2)_n$ R	Thickness (nm) Time (min)			Final etching time (min)	Refractive index at 633 nm (mm)
	0	1	2		
OCH_2CH_3	350	71.9	124	5	1.50
OCH_2CF_3	620	147	322	4	1.33
OC_6H_5	320	17	42.3	14	1.78
OC_6H_4Cl-p	129	32	64	4	1.62
HNC_6H_5	609	24	53	20	1.70
HNC_6H_4Cl-p	498	32	64	14	1.84
LMR	680	31	58	20	1.62

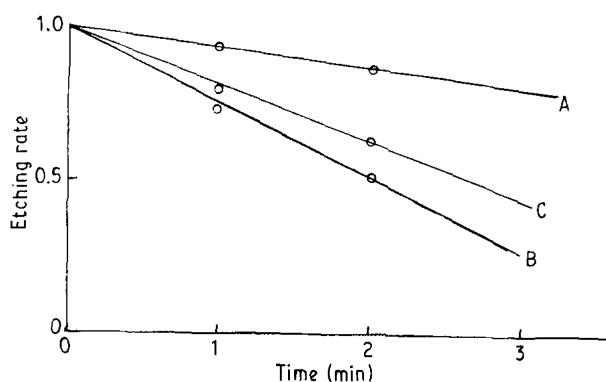

Figure 1 Etching rate of some poly(organophosphazene) films prepared on silicon wafer with plasma (CF_4 40 sccm, O_2 sccm, 5 Pa, 0.08 $W cm^{-2}$). (A $[NP(OC_6H_5)_2]_n$, B $[NP(OC_6H_4Cl\text{-}p)_2]_n$, C $[NP(OCH_2CH_3)_2]_n$)

TABLE II The films of thickness disappeared under the various pressure for 1 min using the plasma (CF_4 40 sccm, O_2 sccm, 0.08 $W cm^{-2}$)

$(NPR_2)_n$ R	Pressure (Pa)		
	1	5	20
OCH_2CH_3	800 A	719 A	740 A
OCH_2CF_3	1030	1470	1490
OC_6H_5	200	170	130
OC_6H_4Cl-p	330	320	280
HNC_6H_5	330	240	240
HNC_6H_4Cl-p	330	320	280
LMR	340	310	210

N_{1s}, C_{1s}, P_{2p} and the Cl_{2p} core signal are also summarized in Table III. The relative atomic per cent of F, O, N, C, P and Cl on films A and B are estimated from the calculation of the peak area as shown in Figs 2 to 5 and the results are given in Table IV.

3.3.1. $[NP(OCH_2CF_3)_2]_n$

In the case of $[NP(OCH_2CF_3)_2]_n$ films, it is found that films A or B give six peaks. The maximum peak of fluorine core signal (F_{1s}) appears at 690.6 and 690.8 eV for films A and B, respectively. The relative atomic per cent of F of film A is similar to that of film B, but the calculated atomic per cent of $[NP(OCH_2CF_3)_2]_n$ is not in accord with them. The maximum peak of oxygen core signal (O_{1s}) appears at 536.1 and 536.2 eV for films A and B, respectively. The relative atomic per cent of oxygen of film B increases about 20% in comparison with that of film A though the spectrum of the film B is broad. This means that the $-OCH_2CF_3$ side chain may be oxidized with plasma. The maximum peak of nitrogen core signal (N_{1s}) occurs 400.6 and 401.2 eV for films A and B, respectively, and the latter peak is shifted to the higher energy side about 0.6 eV. The relative atomic per cent of nitrogen is almost the same in both films A and B. The maximum peak of carbon core signal (C_{1s}) appears at 295.0 and 289.9 eV or 295.3 and 290 eV, respectively, for films A and B. The relative atomic per cent of carbon in film B decreased by about 18% in comparison with that of film A. It is assumed that the carbon atom must be removed with the plasma. The maximum peak of the phosphorus core signal (P_{2p}) also occurs at 136.6 and 136.8 eV for films A and B, respectively. It is found that an increase of relative atomic per cent of P in film B is observed.

3.3.2. $[NP(OCH_2CH_3)_2]_n$

The original film A and film B have five peaks as shown in Fig. 3. The relative atomic per cent of F, O, N, C and P estimated as shown in Table IV are not, however, in accord with the theoretical value. The maximum peak of fluorine core signal (F_{1s}) of the film appears at 688.5 and 688 eV for films A and B, respectively. Although $[NP(OCH_2CH_3)_2]_n$ had no fluorine atoms, the original film A includes about 0.6 at % F and the relative concentration of F of film B is about 5.3 at %. This may be attributed to the reaction between the film and plasma, that is, the film reacts with CF_3^+ or F^- ions originated by the plasma. The maximum peak occurred from the oxygen core signal (O_{1s}) of the films A and B appears at 534.1 eV, but the relative atomic per cent of oxygen of the films A and B are almost the same as that of the film. This means that C–O bond is not affected by the plasma. The maximum peak of nitrogen core signal (N_{1s}) appears at 399.2 and 400.4 eV for films A and B, respectively. The latter peak is shifted to high energy side by about 1.2 eV. The relative atomic per cent of oxygen of film A is also similar to that of film B. The maximum peak

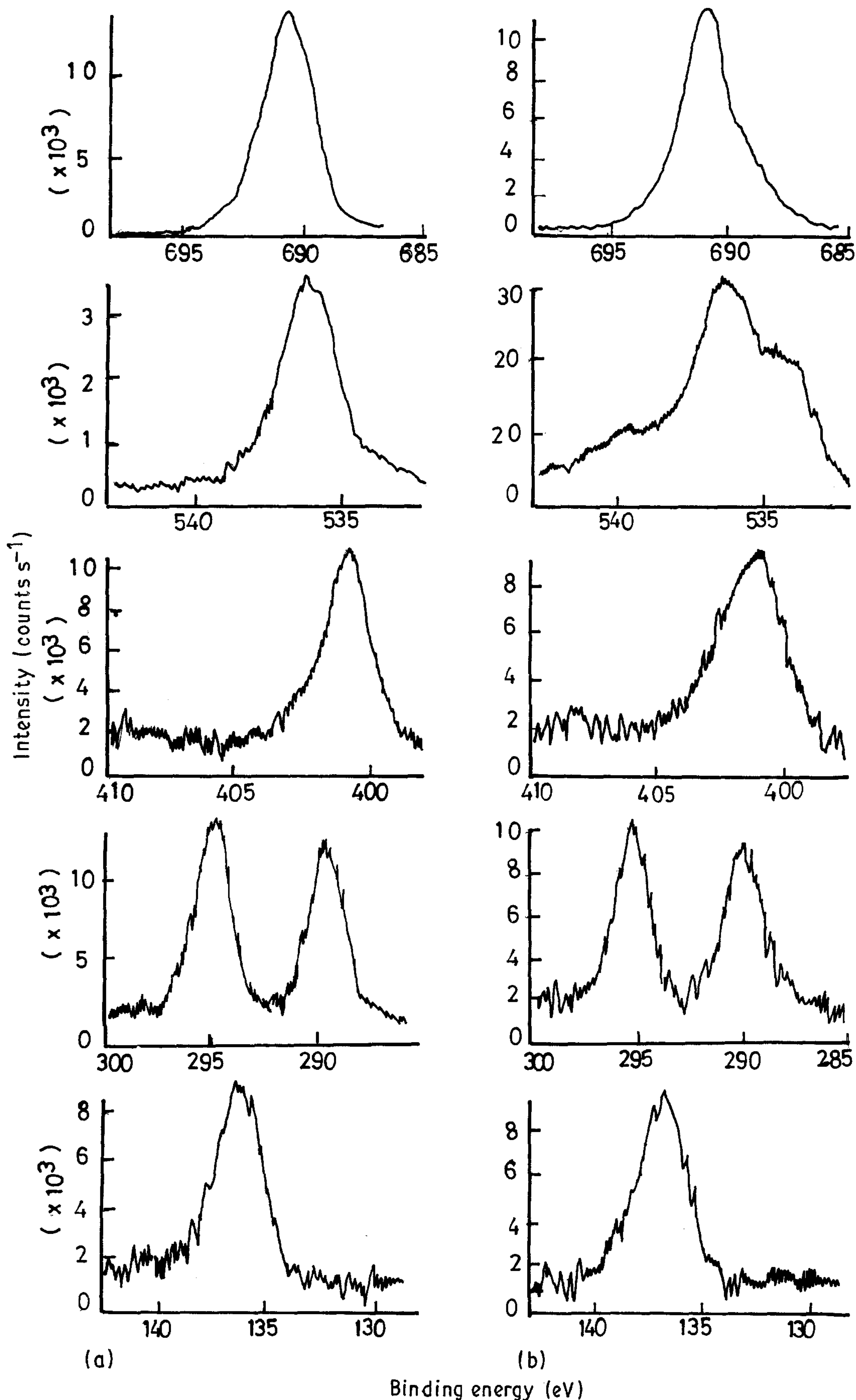

Figure 2 ESCA of poly(bistrifluoroethoxyphosphazene) film (a) without and (b) with plasma.

of carbon core signal of the film A appears at 286 eV, but the relative atomic per cent of carbon of film B is lower than that of the film A by about 18%. This means that carbon atoms must be eliminated with plasma. On the other hand, the maximum peak of phosphorus core signal appears at 135 and 135.3 eV for films A and B, respectively. The relative atomic per cent of phosphorus is similar in both films A and B.

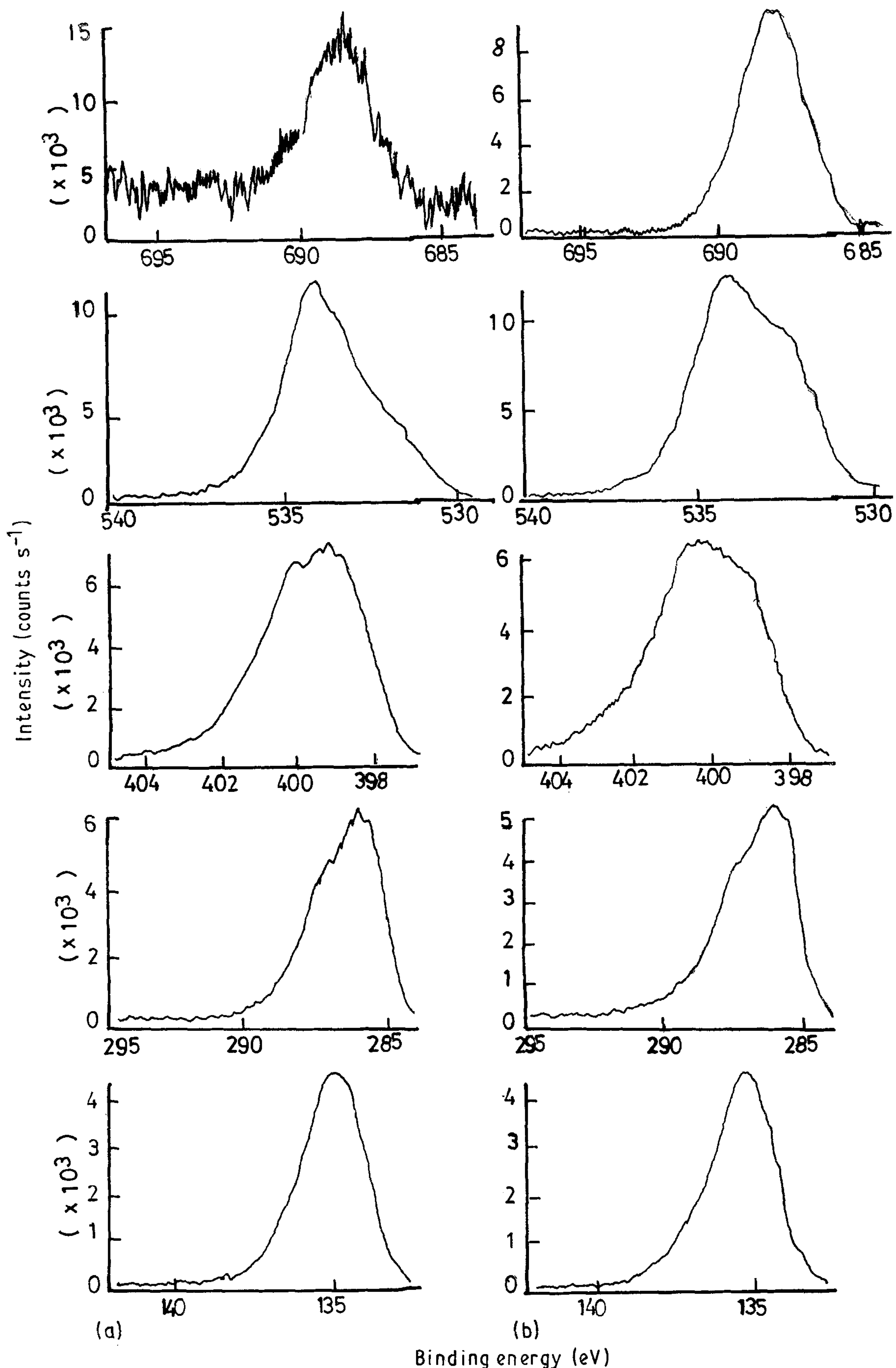

Figure 3 ESCA of poly(bisethoxyphosphazene) film (a) without and (b) with plasma.

Consequently, the NP skeleton of the film is not affected by the plasma or oxygen and the $-OCH_2CH_3$ side chain must be fluorinated with the CF_3^+ or F^- from the plasma. Even if the side chains can be oxidized with plasma, the rate of oxidation of $[NP(OCH_2CH_3)_2]_n$ must be lower than that of $[NP(OCH_2CF_3)_2]_n$, since the former is stable for plasma as shown in Fig. 1.

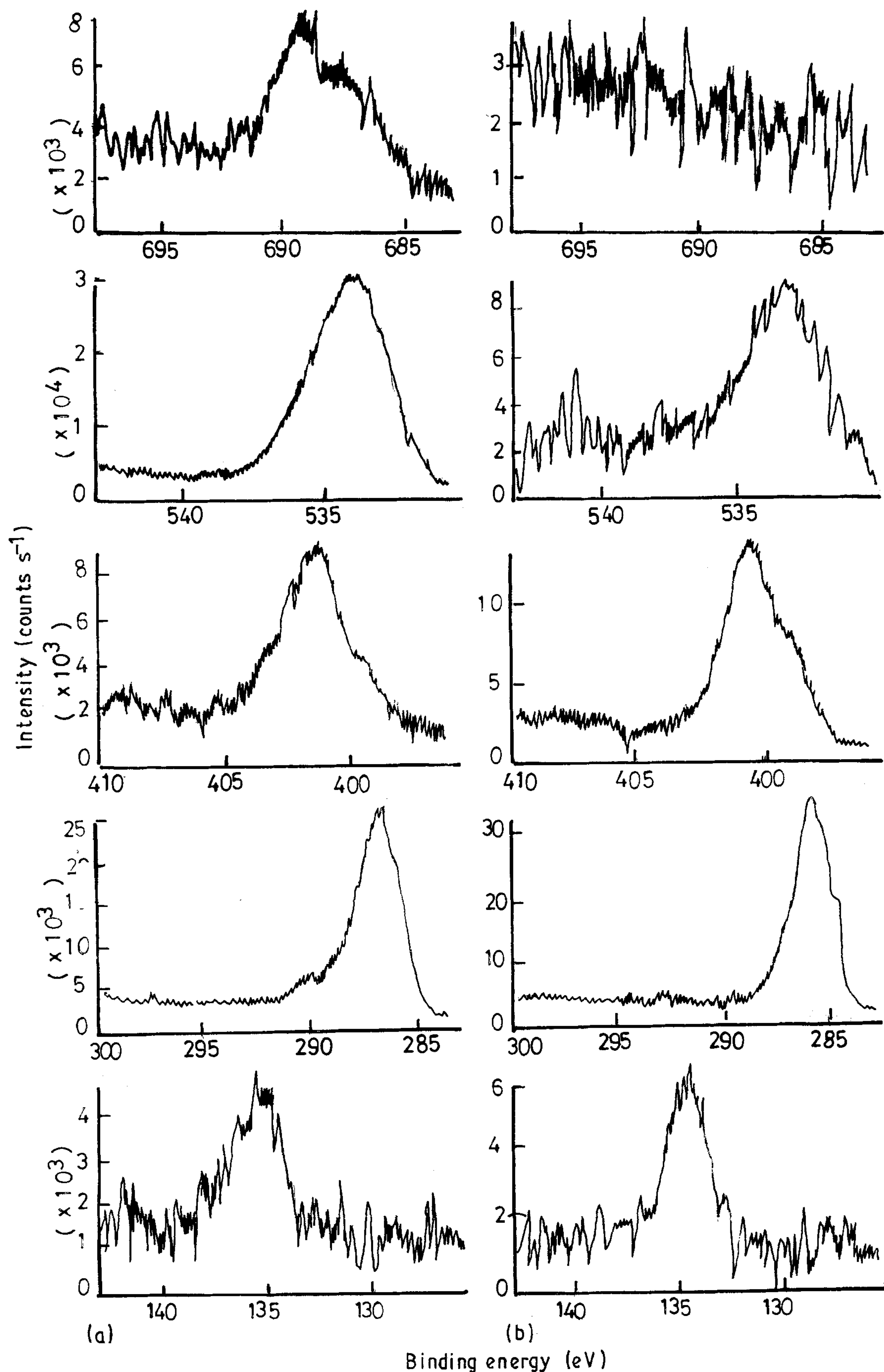

Figure 4 ESCA of poly(bisanilinophosphazene) film (a) without and (b) with plasma.

3.3.3. $[NP(HNC_6H_5)_2]_n$

As for the fluorine core signal (F_{1s}), film A shows a broad peak from 690 to 687 eV. On the other hand, film B shows multiple peaks ranging from 698 to 680 eV. The relative atomic per cent of fluorine is about 3.9 at % in film B as shown in Table IV. Then it suggests that the $-HNC_6H_5$ side chain may react with the CF_3^+ or F^- originating from the plasma (CF_4–O_2). Although this film did not contain oxygen atoms, the maximum peak of the oxygen core signal

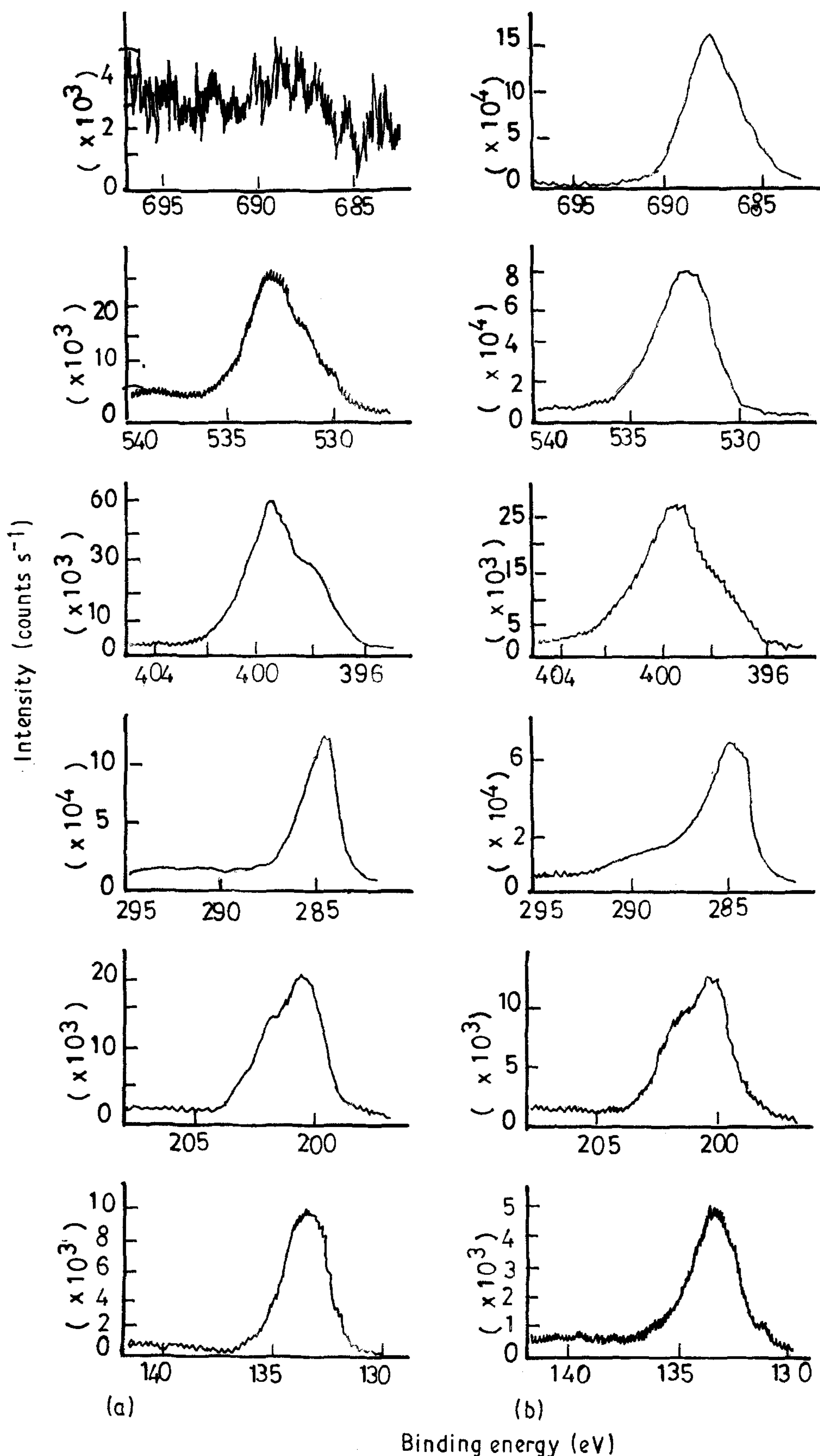

Figure 5 ESCA of poly(bis-p-chloroanilinophosphazene) film (a) without and (b) with plasma.

appears at 533.4 and 534 eV for films A and B, respectively. Generally, it is said that the peak appears near 533 eV can be assigned to C–O, C=O or H_2O. Consequently, this peak belongs to the absorbed water in film A. On the other hand, the relative atomic per cent of oxygen is higher than that of the film A by about 26%. This means that film B must be oxidized with plasma. The maximum peak of the nitrogen core signal appears at 400.4 and 401.4 eV in films A and B, respectively. The latter peak is shifted to the higher energy side by about 1.0 eV and the relative atomic per cent of nitrogen becomes lower by about 43% for film B in comparison with that of film A. As for the carbon core signal, the maximum peak appears at

TABLE III The maximum peak of F_{1s}, O_{1s}, N_{1s}, C_{1s}, P_{2p} and Cl_{2p} core signal

$(NPR_2)_n$ R		F_{1s} (ev)	O_{1s} (ev)	N_{1s} (ev)	C_{1s} (ev)	P_{2p} (ev)	Cl_{2p} (ev)
OCH_2CF_3	(A)	690.6	536.1	400.6	295.0, 289.8	136.6	
	(B)	690.8	536.2	401.2	295.3, 290.0	136.8	
OCH_2CH_3	(A)	688.5	534.1	399.2	286.0	135.5	
	(B)	688.0	534.1	400.4	286.0	135.3	
HNC_6H_5	(A)		533.4	400.4	285.6	134.6	
	(B)		534.0	401.4	286.5	135.5	
HNC_6H_4Cl-p	(A)		532.9	399.5	284.9	133.6	200.3
	(B)	687.8	532.6	399.4	284.7	133.3	200.1

A without plasma, B with plasma

TABLE IV The relative atomic weight per cent of F, O, N, C, P and Cl

$(NPR_2)_n$ R		F (at %)	O (at %)	N (at %)	C (at %)	P (at %)	Cl (at %)
OCH_2CF_3	Cal	42.9	14.3	7.6	28.6	7.1	
	(A)	42.8	17.6	7.1	23.1	9.5	
	(B)	42.1	21.2	7.2	18.9	10.7	
OCH_2CH_3	Cal		25.0	12.5	50.0	12.5	
	(A)	0.6	31.3	15.9	37.6	14.6	
	(B)	5.3	34.3	14.5	31.0	15.0	
HNC_6H_5	Cal			18.8	75.0	6.3	
	(A)		8.7	18.4	62.8	10.1	
	(B)	3.9	26.6	10.5	51.0	8.0	
HNC_6H_4Cl-p	Cal			16.7	66.7	5.6	11.1
	(A)	0.2	3.0	17.3	67.5	5.4	6.6
	(B)	14.8	13.7	12.6	50.4	3.3	5.2

Cal: Calculated values. A without plasma, B with plasma

285.6 and 286.5 eV for films A and B, respectively, due to C–H or C–N bond. The maximum peak of phosphorus core signal also appears at 134.6 and 135.5 eV for films A and B, respectively.

3.3.4. $[NP(HNC_6H_4Cl\text{-}p)_2]_n$

The relative concentrations of nitrogen, carbon and phosphorus except chlorine are in accord with the theoretical values of $[NP(HNC_6H_4Cl\text{-}p)_2]_n$. As for the fluorine core signal (F_{1s}), the original film A has multiple peaks from 698 to 683 eV. The maximum peak appears at 687.8 eV in film B since it must react with the CF_3^+ or F^- ions originated by the plasma. The relative fluorine content is about 14.8 at %. Although the film of $[NP(HNC_6H_4Cl\text{-}p)_2]_n$ did not contain any oxygen atoms, the maximum peak of oxygen core signal (O_{1s}) appears at 532.9 and 532.6 eV for films A and B, respectively. This peak is due to absorbed water in the film. The relative concentration of oxygen is 13.7 at % in film B and higher than that of film A. This means that the film must be oxidized with plasma. The maximum peak of the nitrogen core signal (N_{1s}) appears at 399.5 and 399.4 eV for films A and B, respectively, and the relative concentration of nitrogen in film B decreases about 28 at % in comparison with that of film A. The maximum peak of carbon core signal (C_{1s}) appears at 284.9 and 284.7 eV for film B. There would be no significant changes of the maximum peaks of nitrogen signal (N_{1s}) and phosphorus (P_{2p}) core signal in both films A and B. The relative concentrations in film B is, however, lower than that in film A. This means that the film is not stable for plasma since fluorination and oxidation reaction occurred with the plasma.

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