

# Some Surface Properties of Plasma Polymers Prepared from Hexamethyldisilazane and Diethylaminotrimethylsilane

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## Synopsis

Plasma polymers from some silyl amines were produced by the radio frequency of 13.56 MHz, and the surface properties were investigated. The polymers were revealed to be as hydrophobic as a plasma polymer from tetramethylsilane, which does not contain nitrogen. The hydrophobicity became effective at around 50 Å thicknesses of these polymer layers deposited on micro-slide glass. These polymers have gradually become comparatively hydrophilic with the aging. The change of wettability is probably due to the oxidation of these surface layers to form oxides and peroxides, which are more hydrophilic. The hydrophobic character of silyl amine plasma polymers could be explained by the lack of amines and/or amides in these polymers, as observed with ATR-IR and ESCA spectra. These spectroscopic observations also suggest that nitrogen is a more fragile element in plasma than carbon or silicon in the silyl amines.

## INTRODUCTION

Plasma polymers prepared in glow discharges are highly crosslinked, and the thin films obtained have interesting surface as well as bulk properties.<sup>1</sup> For the uniqueness, plasma polymerization is very useful in modification of plastics. Ultrathin membranes produced with this method have been used for reverse osmosis, and some polymers from nitrogen-containing compounds have shown good results in salt rejection.<sup>2</sup> Plasma polymerization is also effective for the improvement of such polymer surface properties as adhesion and compatibility with organs.

Usually, hydrophilic groups or hydrophobic groups are incorporated in the course of plasma polymerization, and one of the advantages in this method is that the properties can be controlled arbitrarily by the plasma conditions employed, especially the monomer or gas used for the plasma. Plasma polymers from silyl compounds are hydrophobic, and those from nitrogen-containing monomers are hydrophilic.

Plasma polymerization of silyl compounds has been widely investigated not only for the reaction mechanism, but also for the properties of the polymeric films, because the polymers form easily in plasmas to give highly crosslinked and tight membranes.

In this study we report on the plasma polymerization of some silyl amines and discuss the surface properties with respect to the wettability. Because silyl amines contain both silicon and nitrogen, which result in hydrophobicity and hydrophilicity, respectively, the surface properties of these plasma polymers should be interesting. The contact angles of water were measured, and the results are discussed in terms of the functional groups detected by the ATR-IR and the elemental analyses of the surfaces estimated by ESCA.

## EXPERIMENTAL

### Materials

The silyl compounds used for the plasma polymerization in this study were the following: hexamethyldisilazane (HMDSZ),  $(\text{Me}_3\text{Si})_2\text{NH}$ ; diethylamino-trimethylsilane (DATMS),  $\text{Et}_2\text{N-SiMe}_3$ , supplied by Tokyo Chemical Industry Co., Ltd., Tokyo. Tetramethylsilane (TMS),  $\text{SiMe}_4$ , supplied by Merck Co., Ltd.

The monomers were used as supplied but were fully degassed before polymerization.

### Plasma Polymerization Procedure

Plasma polymerization was carried out using glow discharges generated by a radio frequency of 13.56 MHz employing an inductive coupling method. The apparatus used was similar in design to the one reported.<sup>3</sup> Vapor pressure in the system was monitored with a Pirani gauge, model PM-12.

After the reaction chamber, 4.4-cm diameter and ca. 40 cm long, was evacuated up to  $0.1 \times 10^{-3}$  Torr, a monomer vapor was introduced into the chamber at a pressure of  $60 \times 10^{-3}$  Torr through a monomer inlet, which is designed to disperse the monomer throughout the chamber and to make more uniform polymeric films. Flow rates of HMDSZ, DATMS, and TMS were 11.2, 11.5, and 11.0  $\text{cm}^3$  (STP)/min, respectively, at the pressure. They were obtained from the pressure-volume relations using the increasing pressure which is observed when the stopcock of the pumping side is closed in the flow system. The flow rate described here therefore corresponds to the amount of a monomer supplied per unit time.

The reaction was carried out at 50 W so that the glow discharges covered the whole chamber. Plasma polymerization under these plasma conditions was good and effective enough for preparing thin, tight polymeric films.

Deposition rates were obtained by weighing the polymers formed on aluminum foils ( $2.0 \times 2.5$  cm). The rates were as follows:

<u>Plasma polymer from</u>	<u>Deposition rate, <math>\text{mg cm}^2 \times \text{min}^{-1}</math></u>
HMDSZ, $MW = 161$	$1.80 \times 10^{-3}$
DATMS, $MW = 145$	$1.75 \times 10^{-3}$
TMS, $MW = 88$	$1.10 \times 10^{-3}$

Deposition rates were also measured on glass slides, which were used for the contact angle measurements. Although the rates are nearly equal for the two substrates, more accuracy and reproducibility can be obtained on the aluminum foil. This is because the weight of polymer is much less than that on the glass substrate.

The approximate thicknesses of the polymers used in this study were estimated from the deposition rates on aluminum foils and assuming the same on the glass slides.

## RESULTS AND DISCUSSION

## Contact Angle of Water

Contact angles of water were measured on these polymers deposited on micro-slide glasses, using a shadowgraph (model H-14, Nikon Co., Ltd., Tokyo). The water used was distilled and purified before the contact angle measurements.

Figure 1 shows the contact angles on the plasma polymers with various thicknesses of the layers. These samples were obtained by changing the reaction time under the condition described in the Experimental section. The contact angle data were obtained one day after the sample preparation because the values of the contact angle changed with the age and reached the limiting value (see below). The contact angles increased sharply with the thickness of the polymer layers from an initial value of  $25^\circ$  on the nontreated slide glass, and reached the limiting contact angle. The thickness revealing the hydrophobicity in these cases was  $50 \text{ \AA}$ .

The limiting values of the contact angle are shown in Table I. There are no significant differences in the values among these silyl plasma polymers. It is especially interesting to note that the plasma polymers from these silyl amines are as hydrophobic as the one from tetramethylsilane, which does not contain nitrogen. In order to show the effect of the nitrogen contained in a monomer, which plays an important role in the hydrophilicity in the resulting polymer, the contact angles of plasma polymers from benzene, acetylene, pyridine, and acrylonitrile, which were prepared under the same plasma conditions as for the silyl polymers, are also shown in the Table I. The thickness of the polymer layers on the glass substrates was adjusted to approximately  $400 \text{ \AA}$ . As shown, the plasma polymers from nitrogen-containing pyridine and acrylonitrile are more hydrophilic than those from benzene and nitrogen. The hydrophilicity is con-

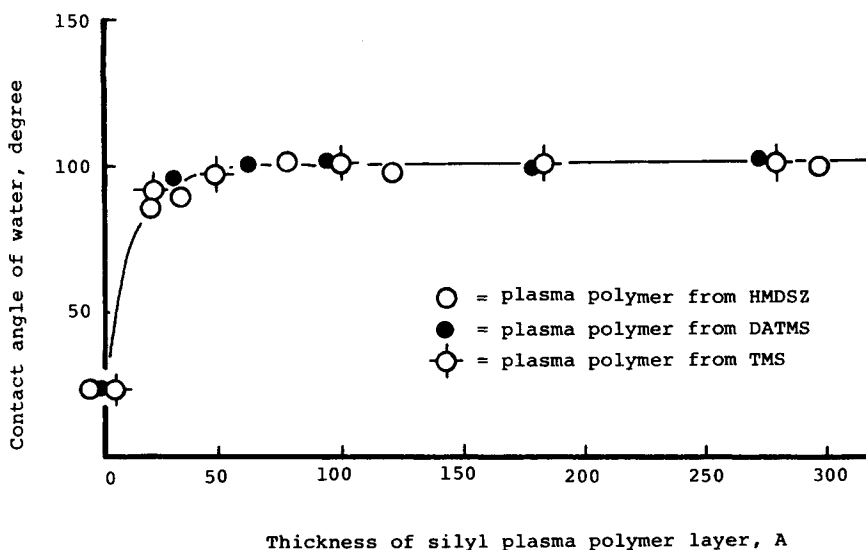


Fig. 1. Dependence of contact angle of water, on the thicknesses of the plasma polymer layers prepared from hexamethyldisilazane (HMDSZ), diethylaminotrimethylsilane (DATMS), and tetramethylsilane (TMS).

TABLE I  
Limiting Values of Contact Angles of Water on Plasma Polymers from Silyl Compounds and Hydrocarbons with and without Nitrogen

Plasma polymer from	Monomer formula	Limiting value of contact angle, deg
HMDSZ	$C_6H_{19}Si_2N$	102
DATMS	$C_7H_{19}SiN$	102
TMS	$C_4H_{12}Si$	100
Acetylene	$C_2H_2$	82
Acrylonitrile	$C_3H_3N$	62
Benzene	$C_6H_6$	84
Pyridine	$C_5H_5N$	60

sidered to be due mainly to the amino groups formed by rearrangement from  $-N=CH-$  and nitrile groups of the monomers under exposure to plasma, and also due to the amide groups successively formed by oxidation of the amines in air. Contrarily, the lack of hydrophilicity in the silyl amine plasma polymers arises from the significant decrease of nitrogen in these polymers, as will be shown and discussed later in the infrared and the ESCA studies.

The contact angles of water on the 400-Å-thick polymers were also measured after aging (Fig. 2). The angles have changed to the limiting values in less than 24 hr, although the time more or less depends on the kind of polymer. It is well known from ESR studies that plasma polymers are very rich in radicals and that the half-lives of the radicals are relatively long even in air.<sup>4</sup> They are considered to react with the oxygen in air, forming oxides and peroxides that are rather hydrophilic. The change of contact angle of water as observed with aging seems to reflect the effects of oxidation.

The aging time dependence of the contact angles was also investigated for the 50-Å samples. Almost similar trends in the change of contact angles have been

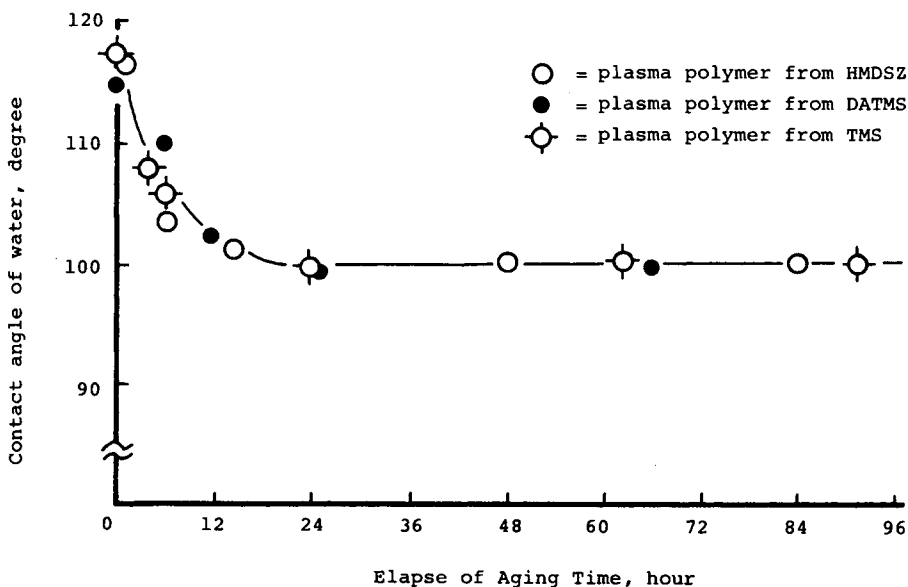


Fig. 2. Change of contact angle of water on the silyl plasma polymers (400 Å) with aging.

observed as in the case of the 400-Å coatings. However, when the polymer layers are thinner, the measurements of the contact angles are not as reproducible. In some cases, especially depending on the location, the angles were close to that on the uncoated glass substrate.

It may therefore be suggested that the plasma polymer layers when first deposited do not exist in the uniform films but as islands, which will be still effective in giving hydrophobicity.

### Infrared Spectroscopic Study

ATR-IR spectra of these polymers deposited on aluminum foils were taken with an infrared spectrophotometer, model IR-430, with an ATR-2A apparatus (Shimadzu Seisakusho Co., Ltd). The spectra are shown in Figure 3, where the plasma polymers HMDSZ, DATMS, and TMS are numbered 1–3, respectively. The polymer samples were prepared under the conditions described in the Experimental section for a period of 30 min.

It is characteristic of these spectra that the peak bands have become broader than those of original monomers. This suggests that the chemical structures of these polymers are more complicated, and such phenomena are quite common in plasma polymers. In addition, we also note the following characteristics of the spectra. In the HMDSZ plasma polymer, the bands of N—H stretching and bending vibrations—observed at 3400 and 1550  $\text{cm}^{-1}$ , respectively, in the monomer—have almost disappeared. This suggests that the N—H groups have broken down in the course of the polymerization. Wrobel et. al.<sup>5</sup> have studied the plasma polymerization of hexamethylcyclotrisilazane, one of silyl amines, at 20 KHz and observed in the infrared spectrum that the amino groups have still remained mostly in the polymer. Indeed, the N—H stretching vibration band has broadened, possibly due to the rearrangement of the amino group. Their observation is quite contrary to what is seen in the present study. The

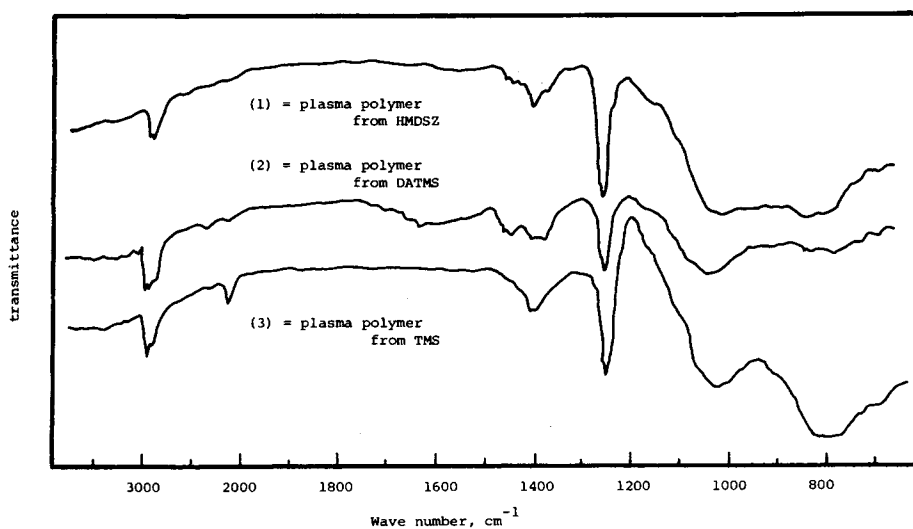


Fig. 3. ATR-IR spectra of the plasma polymers prepared from HMDSZ (1), DATMS (2), and TMS (3) deposited on aluminum foils.

TABLE II  
Peak Positions and Half-Width of the Elements in the ESCA Spectra of Silyl Plasma Polymers

Plasma polymer from	Element	Peak position, eV	Half-width, eV
HMDSZ	C <sub>1s</sub>	285.2	2.2
	Si <sub>2p</sub>	102.5	2.6
	N <sub>1s</sub>	398.5	2.1
	O <sub>1s</sub>	533.1	2.1
DATMS	C <sub>1s</sub>	285.3	2.3
	Si <sub>2p</sub>	102.6	2.6
	N <sub>1s</sub>	400.0	3.5
	O <sub>1s</sub>	532.9	2.2
TMS	C <sub>1s</sub>	285.0	2.4
	Si <sub>2p</sub>	101.5	2.6
	N <sub>1s</sub>	None	None
	O <sub>1s</sub>	532.7	2.3

difference may be due mainly to the polymerization conditions between the two, especially the frequency employed for operating the glow discharges. The frequency used in this study is 13.56 MHz, which is much higher than that the 20 kHz used by Wrobel et al.

Another change in the spectrum is that the 1250 cm<sup>-1</sup> band assigned a trimethyl silyl group has become much smaller in each polymer. The group may participate in the polymerization in plasma, possibly by Si—Si coupling, which is often observed in the reaction of silyl compounds.

Additionally, it is also interesting to note that a band at 2080 cm<sup>-1</sup> has newly appeared in the tetramethylsilane plasma polymer. This band correspond to the Si—H stretching vibration. The group may be formed by the rearrangement of Si—CH<sub>3</sub>. Another interesting feature appearing in the spectra is that all of the silyl plasma polymers have the Si—O—Si and/or Si—O—C bands, which are detected at around 1000–1100 cm<sup>-1</sup> as the stretching vibration. These groups were formed by the oxidation of radically activated species in the plasma polymers.

The skeletons of these polymers are suggested to be highly crosslinked and composed of more Si—C and Si—Si bonds, because the C—H group band around 2960 cm<sup>-1</sup> has become much smaller.

### ESCA Study

In order to make elemental analyses of the surface layers of these silyl plasma polymers, ESCA, which is very effective for this purpose for layers of about 10 Å in thickness, was taken. The polymer samples used for this purpose were prepared by depositing them on aluminum foils under the polymerization conditions described above for a period of 5 min.

Each element appeared much broadly in the ESCA spectra, and the peak positions are shown in Table II.

The relative elemental ratios were obtained from the peak intensities of each element in the spectra, taking the sensitivities into consideration. The sensitivities were given from fluorine compounds by Wagner<sup>6</sup> as follows:

Element	Relative Sensitivity
C <sub>1s</sub>	0.24
N <sub>1s</sub>	0.41
O <sub>1s</sub>	0.61
Si <sub>2p</sub>	0.17
F <sub>1s</sub>	1.00 (as a standard)

Although these values are derived from inorganic fluorides, except for C<sub>1s</sub> (from polytetrafluoroethylene), they are applied to the silyl plasma polymers. The relative elemental analyses were carried out by dividing the peak areas by the sensitivities (Table III). Here, as carbon is selected a standard, the values for C<sub>1s</sub> are taken to be equal to those for original monomers, i.e., 6.0 for HMDSZ and its polymer, 7.0 for DATMS and its polymer, and 4.0 for TMS and its polymer. Consequently, the values for N<sub>1s</sub> and Si<sub>2p</sub> are relative to that of C<sub>1s</sub>.

If the polymer/monomer ratios were taken as shown in the line (3), it is needless to say that the values for C<sub>1s</sub> are 1.0 in each polymer, and then the ratios reveal the changes (or increase or decrease) of the elements in the polymerization compared to C<sub>1s</sub>. Silicon remains three to five times more, and nitrogen decreases by one-third to one-fourth in the plasma polymers compared with carbon. This fact suggests a kind of plasma susceptibility, and it will be concluded that the ease of fragmentation of these silyl compounds in plasma is in the order of N > C > Si.

The amount of gaseous products in plasma can be related to the pressure changes in glow discharges. Pressure in the system, which was adjusted to  $60 \times 10^{-3}$  Torr before plasma exposure, was measured in glow discharges. They reached  $52 \times 10^{-3}$ ,  $54 \times 10^{-3}$ , and  $24 \times 10^{-3}$  Torr for HMDSZ, DATMS, and TMS, respectively, during glow discharges at 50 W and did not change much at up to 150 W. Although the kinds of species generated and present in the plasma states cannot be given exactly at the present stage, the difference in pressure between silyl amines and TMS during glow discharge seems to reflect the liability to fragmentation, i.e., silyl amines contain more breakable portions in plasma than TMS does.

TABLE III  
Elemental Analysis of Silyl Plasma Polymers Estimated by ESCA Peaks

Plasma polymer from	Element	Relative intensity of element		
		Monomer	Plasma polymer <sup>a</sup>	Polymer/monomer
HMDSZ	C	6.0	6.0	1.0
	Si	2.0	5.76	2.88
	N	1.0	0.24	0.24
	O	—	0.24	—
DATMS	C	7.0	7.0	1.0
	Si	1.0	5.04	5.04
	N	1.0	0.35	0.35
	O	—	1.96	—
TMS	C	4.0	4.0	1.0
	Si	1.0	2.88	2.88
	O	—	0.17	—

<sup>a</sup> Estimated by the ESCA peaks taking account of the relative elemental sensitivity.

## CONCLUSIONS

The important aspects described in this paper may be summarized as follows:

1. Plasma polymers from silyl amines are as hydrophobic as the one from tetramethylsilane, and the hydrophobicities are due mainly to the loss of nitrogen (amino and/or amide groups) in the polymers.

2. The hydrophobicity becomes effective in polymer layers around 50 Å thick.

3. The contact angle of water in these silyl plasma polymers decreases gradually with aging, reaching a limit in about 24 hr. That is, the polymers become comparatively more hydrophilic due to oxidation in air that results in oxides and peroxides.

4. A decrease of nitrogen and an incorporation of oxygen in the plasma polymers were observed spectroscopically with ATR-IR and ESCA.

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