The Structure of Organosilicon Plasma-Polymerized Coatings on Metal Substrates

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Synopsis

The structure of coatings formed by the low pressure plasma-polymerization of hexamethyldisiloxane has been studied by FTIR and XPS techniques. The coatings were performed in two pressure regions: 0.63–0.88 and 0.36–0.44 torr. At both pressures much of the structure of the monomer appeared to be maintained. Coatings deposited at the higher pressure showed the expected increase in abstraction of methyl groups and formation of Si — O — Si crosslinks with increasing discharge power. The lower pressure coatings showed a markedly more diverse pattern of peaks associated with Si — O bonds. The spectra of the monomer, hexamethyldisiloxane, and of a highly crosslinked silicone resin were examined in order to clarify the way in which FTIR spectra varied during the polymerization and crosslinking processes. The different structures observed emphasize a considerable potential for tailoring structure by varying deposition conditions.

INTRODUCTION

Plasma polymerization of organic monomers in low pressure glow discharges can produce thin, tough, pinhole free films which have a variety of potential applications. These include uses as permselective membranes, insulating layers in microelectronic components, protective coatings, and laser light guides.[1] However, to date, few of these applications have been developed commercially.

One of the characteristic features of plasma polymerization is the ability to initiate polymerization of organic compounds which will not form polymers under normal polymerization conditions. Recently considerable attention has been devoted to the plasma polymerization of organosilicon monomers, particularly hexamethyldisiloxane (HMDSO). These monomers are of interest because of high deposition rates and the ability to control structure and properties by varying deposition conditions.[2]

The deposition of films from HMDSO in microwave and radio frequency (RF) discharges was reported by Wrobel et al.[3] and the films analyzed by infrared spectroscopy and density measurements. The films appeared to consist primarily of a dense phase consisting of highly crosslinked and substantially "inorganic" polymer, with a thin oligomeric surface layer. Microwave discharges tended to produce higher levels of crosslinking than did

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radio frequency discharges. Deposition rates and densities tended to increase with higher substrate temperatures[4] and discharge power.[2] This structural pattern has been confirmed by Tajima and Yamamoto,[5] using a combination of IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and solid-state NMR.

The published work only provides limited information on the effect of deposition conditions on the structure and properties of plasma-polymerized layers. The discharge power, frequency, monomer flow rate, and pressure, as well as the geometry of the deposition chamber, can all have an effect on the deposition process. The present work was concerned with establishing the most appropriate conditions for depositing a protective film[6] on vacuum-deposited thin films of Co_4Ni or Co_3Cr. Such films are of interest because of
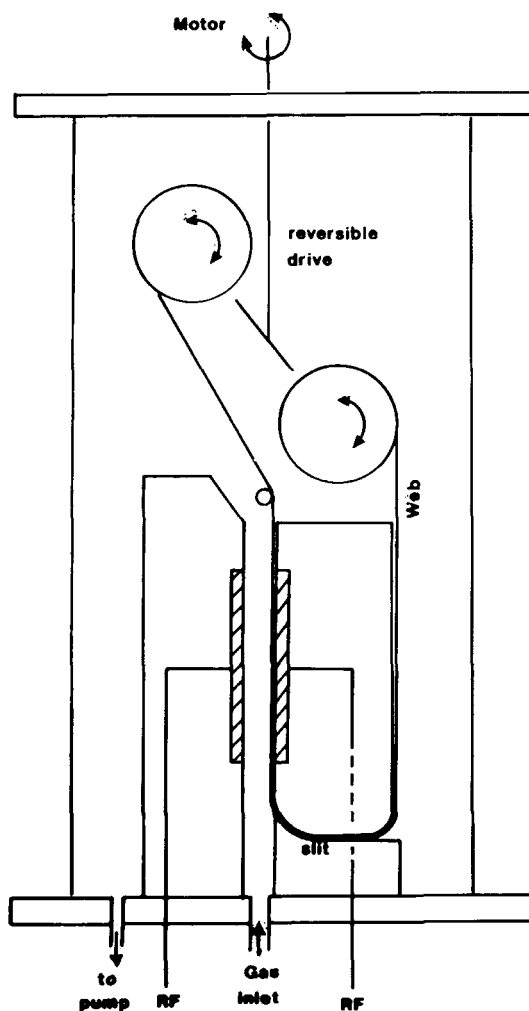

Fig. 1. Schematic diagram of the plasma reactor.

potential application in high density magnetic recording. The structure of the polymerized layer was studied by IR spectroscopy and, to a limited extent, by XPS.

EXPERIMENTAL

The reactor (Fig. 1) consisted of a vertical glass cylinder containing two vertical electrodes. The electrodes were confined on either side to constitute a rectangular space through which the vapor flowed upwards past the electrodes. The substrate was held in contact with one electrode.

The HMDSO monomer vapor was fed into the reaction chamber through a MKS flow metering and control system which had a flow range of $0-100 \, cm^3/min$ (STP). The pressure in the chamber was measured by a MKS Baratron 310 temperature controlled sensor and regulated by a combination of flow rate and throttle valve settings. The discharge was created by a 700 kHz oscillator.

The substrates were vacuum evaporated metal alloys on polymer: Either Co_3Cr on polyimide or Co_4Ni on polyester. The plasma-polymerized films were deposited on these substrates to thicknesses in the region of 50–200 nm. Strong, distinct interference colors were obtained by plasma coating onto the smooth, highly reflecting metallized substrates. The colors and the fringes at the extremities of the coatings were used for obtaining thickness estimates. In contrast to most published studies, our deposition experiments were performed onto moving substrate web, thus enabling coating under stable plasma conditions without the vagaries of startup and shutdown of plasma.

Infrared spectra were obtained using a Perkin-Elmer 1710 Fourier transform infrared (FTIR) spectrophotometer with a multiple attenuated total reflectance attachment and a 3600 data station. Spectra were obtained of the substrates with and without the plasma-polymerized layer. Difference spectra were derived by means of the data station and proprietary software.

The XPS studies of the polymer films were performed by L. Gerenser in the Kodak Research Laboratories, Rochester, NY.

RESULTS

Two series of coatings were selected for the infrared spectra studies. Details of these are given in Table I. Basically the coatings were performed at two pressure levels, ca. 0.8 and 0.4 torr, with corresponding flow rates, and a considerable range of plasma power. Although voltages were lower in the second series, the power range was similar in the two series.

Before examining the infrared spectra of the polymer films, it is worth considering the major features of the HMDSO monomer spectrum, particularly the $1500-600 \, cm^{-1}$ region, which contains the principal peaks (Fig. 2). The most significant peaks are the $SiCH_3$ deformation peak at $1260 \, cm^{-1}$, the Si — O — Si vibration peak at about $1070 \, cm^{-1}$, and the $Si(CH_3)_3$ stretching peaks at 850 and $760 \, cm^{-1}$.[7]

The spectra of the polymerized layers varies somewhat with deposition conditions. Coating 1.6 (Fig. 2) shows a broadening of the Si — O — Si band, with a maximum at about $1120 \, cm^{-1}$, and a new peak at $800 \, cm^{-1}$. The latter

TABLE I
Deposition Conditions of Plasma-Polymerized Coatings

Coating no.	Substrate	Power (W)	Pressure (torr)	Flow rate (cm^3/min, STP)
1.1	CoCr/Polymide	15.6	0.63	16
1.2		15.5	0.66	10
1.3		15.5	0.80	15
1.4		18.5	0.80	15
1.6		23.0	0.88	15
1.7		18.5	0.88	15
1.8		14.6	0.88	15
7.8	CoNi/Polyester	8.1	0.36	6
7.9		13.3	0.39	6
7.10		13.3	0.39	6
7.11		17.3	0.40	6
7.12		17.1	0.40	6
7.13		23.3	0.43	6
7.14		23.3	0.44	6

is due to $Si(CH_3)_2$ stretching vibrations, which arise as one of the methyl groups is eliminated during the polymerization process.[3] When plasma power is reduced, while maintaining the same pressure and flow rate, the Si — O — Si peak is somewhat narrower, presumably reflecting a lower degree of crosslinking via silicon atoms (Fig 3).
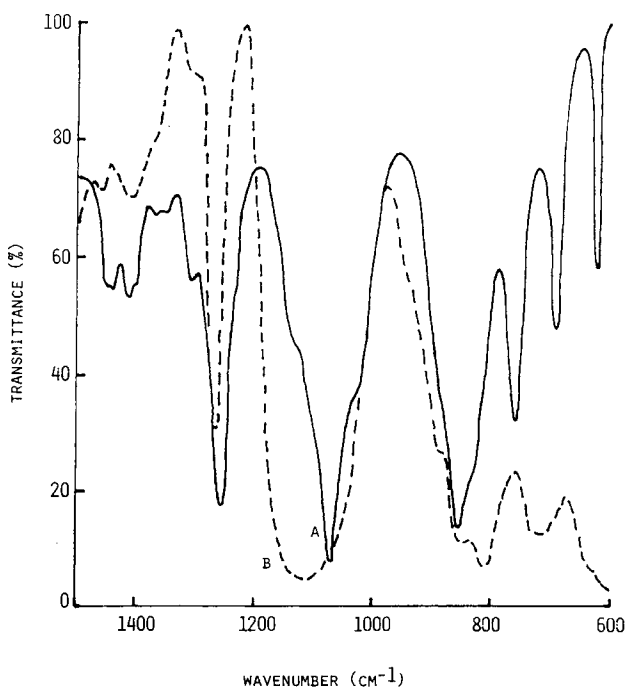

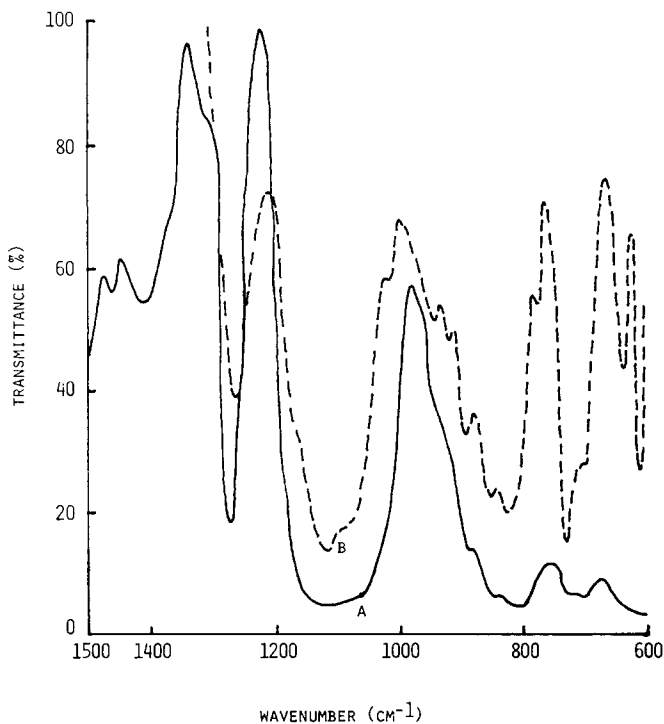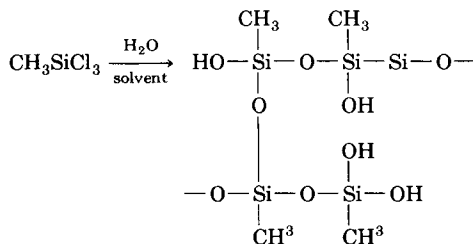Fig. 2. Spectra of (a) HMDSO and (b) coating 1.6.

Fig. 3.   Spectra of coatings (a) 1.6 and (b) 1.7.

Another series of coatings, performed at lower pressures (about 0.4 torr), exhibits a somewhat different pattern. At lower power levels much of the monomer structure appears to be retained, but with the 800 cm^{-1} peak also observed in series 1, and a new peak in the region of 1200 cm^{-1} not previously observed (Fig. 4). Increasing power does not produce a broad band in the 1200–1000 cm^{-1} region, as in the first series. Instead, new peaks appear at 1100 and 1000 cm^{-1} and the peak near 1200 cm^{-1} increases substantially in intensity (Fig 5).

To assist interpretation of the infrared spectra, a study of a silicone resin was also performed. Commercial silicone resins are commonly prepared by cohydrolysis of mixed organochlorosilanes, followed by a partial cocondensation of the resulting silanols, e.g.,

$$\text{CH}_3\text{SiCl}_3 \xrightarrow[\text{solvent}]{\text{H}_2\text{O}}$$

The resulting polysilanols are metastable in solution at room temperature, but
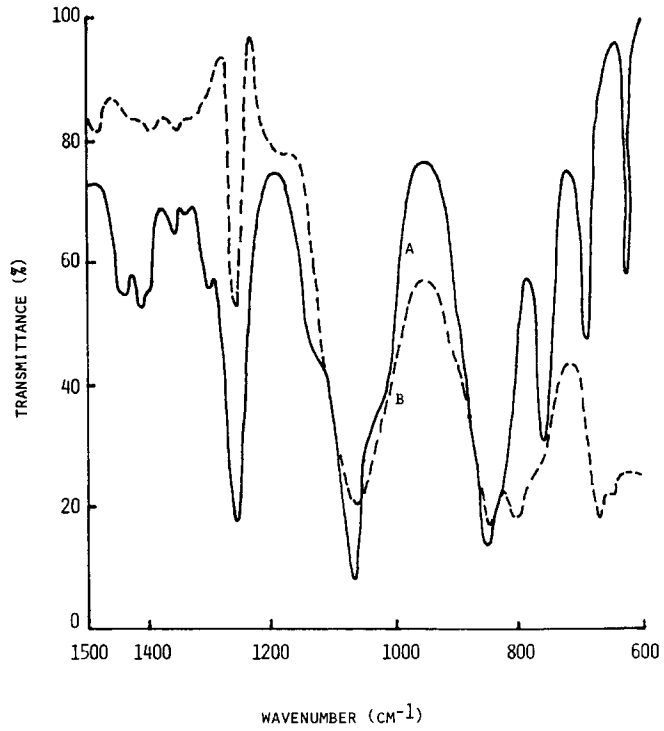
Fig. 4.   Spectra of (a) HMDSO and (b) coating 7.11.
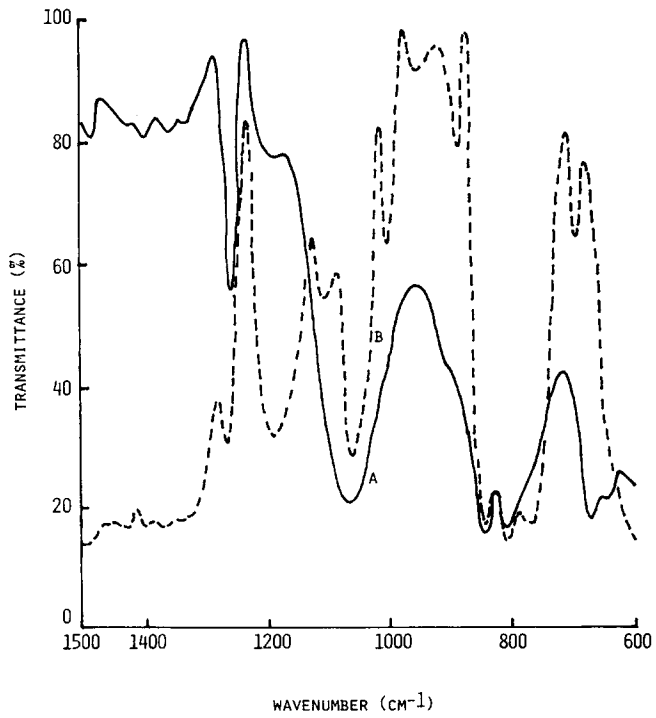

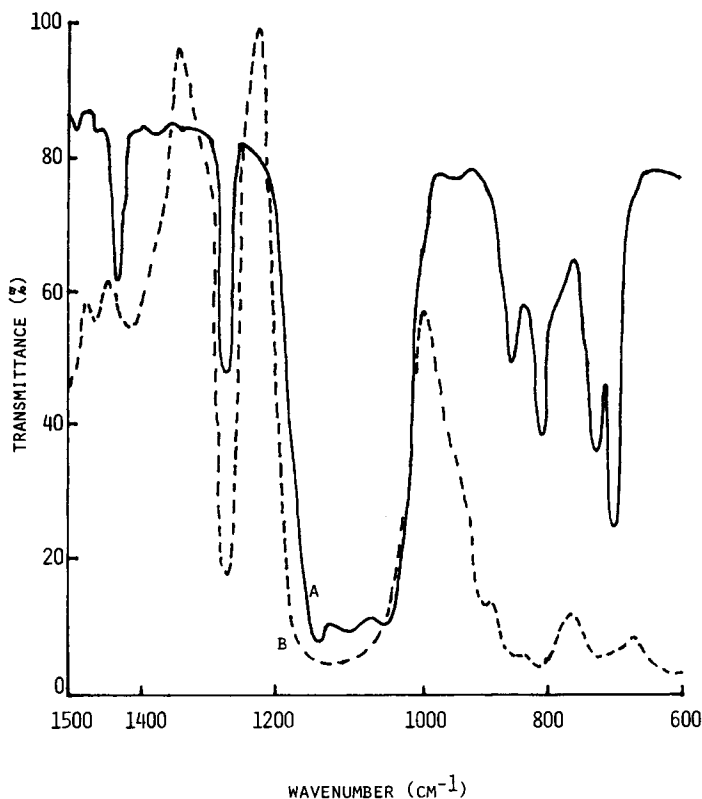Fig. 5.   Spectra of coatings (a) 7.11 and (b) 7.14.

Fig. 6.   Spectra of (a) silicone resin and (b) coating 1.6.

if the solvent is evaporated and the residual material subjected to heat, further condensation occurs and a highly crosslinked polysiloxane is produced.[8]

A Dow Corning 806A silicone resin was coated on a KBr disc, cured at 160°C for 1 h, and its infrared spectrum recorded (Fig. 6). The result, which represents a high degree of crosslinking via Si — O — Si bonds, is similar to the first series, e.g., coating 1.6, and supports the interpretation of the broad band in the 1200–1000 cm^{-1} regions as highly crosslinked Si — O — Si networks.

A most interesting feature of the HMDSO plasma polymer films was the absence of the carbonyl functionality that usually is observed prominently in IR spectra of plasma polymer films even from monomers not containing a C = O group, or no oxygen at all. Carbonyl functionalities may be incorporated into the film as a result of monomer rearrangement, incorporation of adventitious oxygen and water in the plasma, and post-deposition reactions on atmospheric exposure. In the last case, it is thought that residual radicals trapped in the rigid polymer matrix scavenge diffusing oxygen.[1,9] In our arrangement of plasma coating onto moving substrate web comprising a plastic layer, water, and oxygen may be supplied to the deposition atmosphere by residual desorption from and outgassing of the web in spite of extended pumping and wind/rewind transport of the web under vacuum prior to deposition.
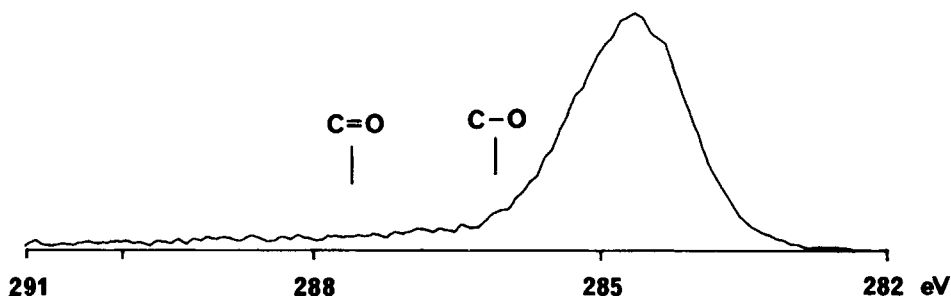
Fig. 7.   XPS C 1s peak of coating 1.7, and expected peak positions for species indicated.

XPS analysis of coatings 1.6 and 1.7 confirmed the absence of $C=O$ functionalities. Furthermore, the C 1s peak was only very slightly asymmetrical to the high energy side (Fig. 7); thus, any contribution due to $C-O$ would have to be very small. Yet, XPS analysis also showed a substantial increase in the O content. The Si 2p peak indicated formation of additional $Si-O$ bonds on plasma polymerization. By deconvolution, the ratio was estimated of the number of Si atoms bound to one O only, as in the monomer, and to more than one O. The ratio was 1 to 3.1 at an RF power input of 7.7 W, and 1 to 1.4 at 6.2 W. In view of the extensive overlap, these ratios must be considered to be very approximate only. Nevertheless, they are consistent with increased formation of additional $Si-O$ bonds at higher power input, due to more extensive monomer breakdown.

The XPS spectra did not allow elucidation of details regarding Si bound to several O. NMR work by Tajima and Yamamoto[5] on plasma polymers, albeit deposited at substantially higher power, showed the presence of two, three, and four oxygen neighbors on Si, with the most frequent combination being two $Si-O$ bonds on one Si.

Consistent with the formation of new $Si-O$ bonds, XPS showed a reduction in the ratio C/Si from the value of 6 of the monomer, indicating that methyl abstraction was an important fragmentation process. Film 1.6, which was deposited at higher power, showed a lower value for C/Si than film 1.7, as expected if the $Si-$ methyl bond is among the more vulnerable to electron impact dissociation.

When comparing information obtained by ATR-IR and XPS, it must be remembered that the penetration depths differ substantially: That of ATR-IR is about 2 μm whereas XPS probes the top 10 nm at most. Nevertheless, comparison is valuable to obtain a qualitative assessment of possible differences in composition of the "surface" (top 10 nm) and the bulk of the plasma polymer film. Our data are not sufficient for detailed comparison, but they indicate that the same basic features are present and no major bonding structure is exclusive to the surface.

DISCUSSION

The infrared and XPS spectra of the series 1 coatings suggest behavior broadly consistent with that found in previously published work, although our

XPS data argue against the C—O bonds shown in Tajima and Yamamoto's hypothetical structure of HMDSO plasma polymer films.[5] However, solid-state NMR and elemental analysis were not available to provide a more detailed analysis for the bulk polymer in the present work. Comparisons with the HMDSO monomer and with highly crosslinked silicone resins tend to confirm mechanisms involving loss of methyl groups and crosslinking via $Si-O$ bonds with increasing discharge power.

However, series 7, performed at lower pressures, presents a somewhat different picture. The clearly defined peaks in the 1000–1200 cm^{-1} region suggest the formation of distinct species rather than the highly crosslinked network formed at higher pressures. The limited analytical tools available in this study prevent a more detailed analysis of the structure of these films, but the results obtained indicate the possibility of tailoring the molecular architecture of these polymeric layers by the careful selection of deposition conditions.

Plasma polymerization in many instances has been found to be quite nonspecific and nonselective, producing random structures of the polymeric network, as a result of extensive, indiscriminate bond breakages in the monomer and re-formations in the polymerization process. Our data indicate, however, that for HMDSO, at least in the low power region we used, there is an unexpected, high selectivity. It appears that methyl abstraction is the dominant process in monomer fragmentation, with the usually observed H loss ($C-H$ bond breakage) of lesser importance. Oxygen then reacts quite selectively, with the free valency on Si, but not on C. The $-Si-CH_2 \cdot$ functionalities produce very few, if any, $Si-CH_2-O$ ether linkages; formation of $Si-CH_2-Si$ crosslinks and $Si-CH_2-C$ (H_2 or H_3) structures may occur, but our data do not enable discrimination between them.

To summarize, HMDSO plasma polymers can be visualized as consisting of an extensively crosslinked structure of organosilicate nature. The network is based largely on $Si-O$ bonds, thus giving an inorganic, silicate-type back-bone, with possible contributions by $Si-CH_2-Si$ and $Si-CH_2-CH_2-Si$ crosslinks, but not $Si-CH_2-O-Si$. Pendant methyl and trimethylsilyl groups abound. The $O-Si-O$ crosslink density relates to plasma power, as does the extent of C (methyl) loss.

Thus, the extent of methyl abstraction from a particular Si atom and consequent formation of additional $Si-O$ linkage appears to be a random, power-dependent process (producing a statistical distribution of one to four oxygen neighbours), but the lack of corresponding formation of bonds by O with free valencies of C is surprising, and we have at present no explanation for this selectivity.

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