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A. M. Wróbel[a,b]; M. R. Wertheimer[a]; J. Dib[a]; H. P. Schreiber[a]
[a] Departments of Engineering Physics and Chemical Engineering Ecole Polytechnique, Canada [b] Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Lodz, Poland

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Polymerization of Organosilicones in Microwave Discharges

A. M. WRÓBEL,* M. R. WERTHEIMER,[†] J. DIB, and
H. P. SCHREIBER

Departments of Engineering Physics and Chemical Engineering
Ecole Polytechnique, C. P. 6079
Station A
Montreal, P. Q., H3C 3A7 Canada

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ABSTRACT

Plasma polymerization of hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSZ) monomers has been carried out in audio- (2 kHz, 20 kHz), radio- (5 MHz), but principally in microwave (2.45 GHz) frequency discharges. Film growth kinetics on glass and aluminum substrates have been studied by thickness and gravimetric measurements; the combined data have led to precise determinations of the film densities. The density data, in turn, provide strong evidence for a hitherto unreported structural feature, namely, that films are composed of a dense solid phase, and a thin (~ 500 Å) "oligomeric" surface layer. The solid component is about 70% denser than the equivalent "conventional" polymer, and has a marked inorganic character, as revealed clearly by infrared spectroscopy. IR analyses of polymers produced in lower frequency discharges tend to show narrow, well resolved absorption bands. In the case of 2.45 GHz films, on the other hand, bands corresponding to "inorganic" linkages tend to become broader and more intense,

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*Present address: Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Boczna 5, 90-362 Lodz, Poland.

[†] To whom correspondence should be addressed.

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and structural features become smeared-out. This is indicative of extensive crosslinking and of the inorganic structural content already mentioned. These results indicate intense fragmentation of monomer molecules in the microwave plasma, as also substantiated by pressure-rise measurements. Radical species created by abstraction of hydrogen, methyl, or other groups are responsible for film formation and growth and for crosslinking reactions within the film.

INTRODUCTION

Among the numerous monomers which have been used for plasma polymerization, the organosilicones were found to form films of rather unique properties which are promising for various practical applications: plasma-polymerized organosilicon thin films, owing to their excellent thermal [1, 2], dielectrical [3, 4], and optical [5-7] properties, may find use as protective coatings and encapsulants, as dielectrics in microelectronics, as antireflection coatings in conventional optics, and as thin film light guides in integrated optics, to name a few examples.

Published data pertain exclusively to studies of organosilicon films deposited by audio- (kHz) and radiofrequency (MHz) discharges. Very little has been published on the structure and properties of plasma-polymer films formed in microwave discharges; among the few existing papers on microwave plasma polymerization [8-10] none has so far dealt with organosilicon films. Furthermore, there are very few published data on the effect of discharge frequency upon plasma polymerization. The discharge frequency seems, however, to be an important parameter which may have significant influence on the kinetics of film deposition, its chemical structure, and physical properties [11].

The present paper describes studies of the kinetics of polymer film growth in microwave discharges by using organosilicon monomers, namely hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSZ)

$Me_3Si{-}O{-}SiMe_3$ (HMDSO) $Me_3Si{-}NH{-}SiMe_3$ (HMDSZ)

We report density measurements obtained on these polymer films, as well as the evolution of the density during polymerization. The effect of discharge frequency and of power density in the plasma on their chemical structure is also discussed.

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EXPERIMENTAL

Plasma polymerization was carried out in a large-volume microwave plasma generator (LMP) operating at 2.45 GHz; the main features of this apparatus have already been described elsewhere [12].

In order to carry out some comparative studies of the effect of frequency, some additional plasma polymerization experiments have been done in audio- and radiofrequency apparatus with electrodes. Care was taken during all these experiments to ensure otherwise similar conditions (pressure, monomer feed rate, power density in the plasma).

In the LMP apparatus, the plasma was generated in a cylindrical, 32 mm diameter quartz reactor having a concentric cooling jacket for forced air flow. Prior to polymerization, the reactor was evacuated to $\sim 10^{-3}$ Torr by a two-stage mechanical pump (Leybold Heraeus, Model D30A), following which the monomer vapor was introduced continuously from a calibrated reservoir, so as to maintain a steady dynamic pressure of 0.2 Torr and a liquid monomer flow rate of 0.05 cm^3/min.

The pressure in the reactor was measured (and in some instances recorded), using a mechanical pressure gauge (MKS Baratron, Type 170M). Stable microwave plasmas were obtained with a minimum absorbed power of about 200 W, resulting in a power density in the plasma of $\sim$ 0.6 W/cm^3, but in some instances experiments were conducted at higher microwave power densities (up to $\sim$ 2.5 W/cm^3). In order to minimize possible substrate heating during film growth, microwave power was applied in 5-sec pulses, with 10-sec intervals between pulses.

Polymer films were deposited on two types of substrates: Al foil, and 14 cm × 3 cm Corning cover glass slides. Film thickness measurements were carried out interferometrically by using a Sloan Angstrommeter (Model M-200); film deposition rates were also monitored gravimetrically by using an electronic digital microbalance (Sartorius, Model 2600).

Infrared spectra were obtained from polymer films on the Al foil substrates by using a Perkin-Elmer 467 spectrophotometer; the multiple internal reflection (MIR) and attenuated total reflection (ATR) techniques were used throughout.

Finally, hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSZ) monomers of spectral grade (PCR Research Chemicals Inc.) were used without further purification. The boiling points and densities (at 20°C) are 99°C and 0.7636 g/cm^3 for HMDSO, and 126°C and 0.7742 g/cm^3 for HMDSZ.

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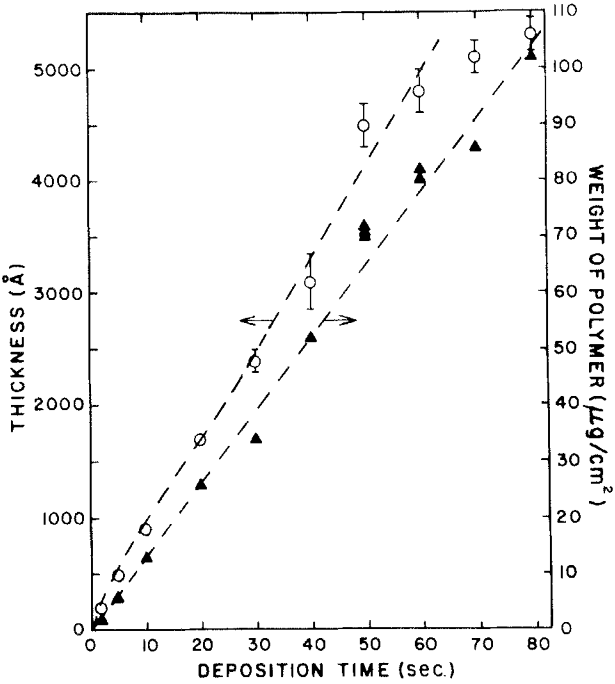

FIG. 1. Plots of (○) polymer film thickness and (▲) weight per unit area as a function of deposition time for plasma-polymerized hexamethyldisiloxane (PP-HMDSO).

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RESULTS

Kinetics of Deposition and Pressure Variations

The kinetics of polymer film deposition was studied by measurements of film thickness, and of the weight of polymer after different discharge durations. The mean film thickness and the weight of polymer per unit area as functions of the discharge duration for films of plasma polymerized HMDSO (PP-HMDSO) and PP-HMDSZ are shown in Figs. 1 and 2, respectively. Thickness and weight per unit area are seen to increase with deposition time t in a complex manner. As will be discussed further below, systematic deviations from apparent initial linearity having important physicochemical implications exist for deposition times up to about 20 sec. The more pronounced nonlinearity in the thickness curves at higher deposition times are presumably caused by partial degradation of the polymer under these

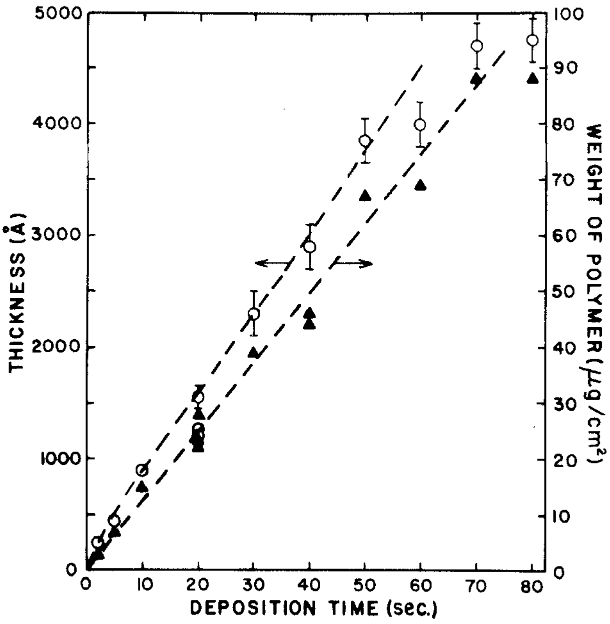

FIG. 2. Plots of (○) polymer film thickness and (▲) weight per unit area as a function of deposition time for plasma-polymerized hexamethyldisilazane (PP-HMDSZ).

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conditions. The values of mean deposition rates in the quasi-linear portions of the thickness and weight curves are listed in Table 1.

The very similar deposition rates noted for both monomers presumably arise from their similar physical and structural features which determine the susceptibility of a monomer for plasma polymerization.

The organosilicon monomers used in this study, normally quite inert towards conventional polymerization, can be readily polymerized in a plasma by reactions involving the abstraction of hydrogen atoms or methyl groups which are liberated to the gas phase [1, 2]. This process, of course, gives rise to a pressure change in the reaction system during discharge. Such pressure variations under steady-state conditions (constant monomer feed rate, constant microwave power applied at t = 0) have been recorded, and are shown in Fig. 3. The pressure in the reaction system is seen to rise quite nonlinearly, reaching a steady value after about 10 sec. The sharp early pressure rise is presumably related to rapid initial fragmentation, the nature of which then evolves and stabilizes with time. A measure of the extent of steady-state monomer fragmentation is the ratio p_d/p_0,

TABLE 1. Deposition Rates and Pressure Change under Experimental Conditions Described in the Text

Monomer	Deposition rate Å/min	Deposition rate $\mu g/cm^2$-min	Pressure change p_d/p_0
Hexamethyldisiloxane (HMDSO)	5200	78	1.99
Hexamethyldisilazane (HMDSZ)	4500	74	1.91

where p_d and p_0 are the steady-state pressure values during and before microwave discharge, respectively. As shown in Table 1, this ratio is close to 2 for the present experimental conditions, suggesting very strong monomer fragmentation and, presumably, a high concentration of chemically active species in the microwave plasma. The shapes of the curves in Fig. 3 further suggest that the chemistry of polymerization may evolve with discharge time. Evidently, since all our polymerizations were carried out by a series of 5-sec pulses, the plasma was never under steady-state conditions. These points will be discussed further in a subsequent section.

Finally, it is interesting to note that no "powder" was ever produced in the microwave discharges, even at high power density (~ 2.5 W/cm^3), whereas at 20 kHz "powder" readily formed at power densities exceeding ~ 0.1 W/cm^3, other conditions being comparable.

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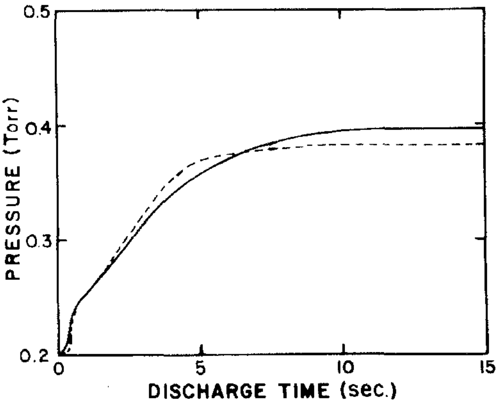

FIG. 3. Pressure change during microwave discharge in vapors of (—) HMDSO and (- -) HMDSZ.

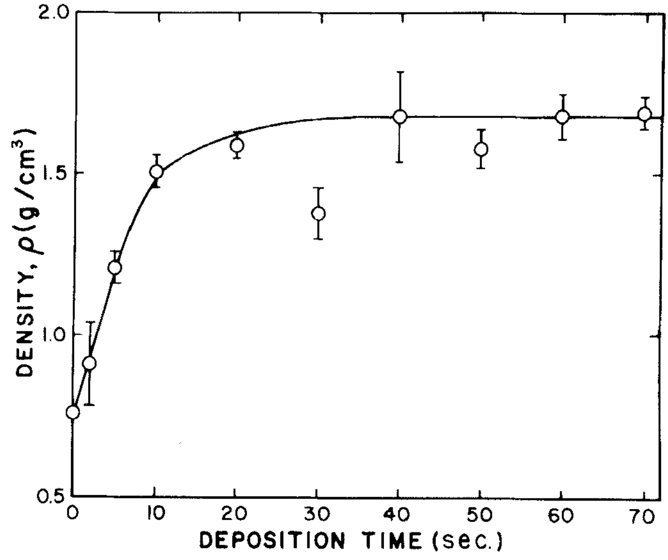

FIG. 4. Mean density of PP-HMDSO films as a function of deposition time.

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Polymer Density Determinations

Independently determined gravimetric and thickness data being available for the polymer films (Figs. 1 and 2), it was possible to calculate their densities. This was done for sets of experimental data pertaining to each of the deposition times in Figs. 1 and 2, by dividing the precise numerical values of the weight of polymer per unit area by its corresponding thickness. The resulting density values of PP-HMDSO and PP-HMDSZ are shown as a function of deposition time in Figs. 4 and 5, respectively. These figures show very clearly that the film density rises, reaching a "plateau" value of about 1.7 g/cm^3 after a deposition time of roughly 20 sec; the data points for $t = 0$ correspond to the density of the liquid monomer. The "pre-plateau" (deposition time $\lesssim$ 20 sec) parts of Figs. 4 and 5 clearly indicate the systematic deviations from linearity in Figs. 1 and 2, mentioned above. The "plateau" density of PP-HMDSO (1.68 g/cm^3) is higher than the density of "conventional" polymethylsiloxane (0.98 g/cm^3) [13] by a factor of ~ 1.7; the reasons for this will be discussed below. A similar comparison cannot be made for PP-HMDSZ for lack of data on "conventional" polymethylsilazane.

By inspecting Figs. 4 and 5, one notes that the "plateau" is attained more rapidly in the case of PP-HMDSZ than for PP-HMDSO. This is

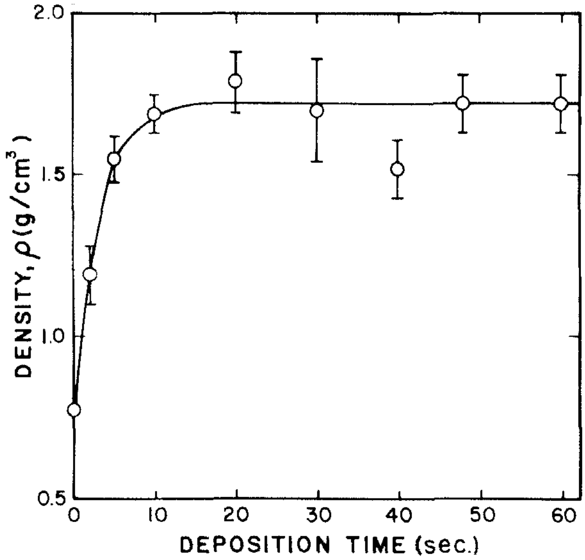

FIG. 5. Mean density of PP-HMDSZ films as a function of deposition time.

shown clearly in Fig. 6, where $\Delta\rho/\rho_0$ is plotted versus deposition time, ρ_0 being the liquid monomer density and $\Delta\rho$ the difference between this latter value and the plasma-polymer density corresponding to the particular deposition time.

Finally, the "plateau" density of thick PP-HMDSO films deposited in a 5 MHz discharge was determined and found to be 1.16 g/cm^3. This result and its relation to those for 2.45 GHz films will also be discussed further below.

Effect of Discharge Frequency on Infrared Spectra

Infrared spectra have been obtained for plasma-polymer films produced in discharges covering a very broad frequency range, namely at 2 kHz, 20 kHz, 5 MHz, and 2.45 GHz. The infrared spectra of PP-HMDSO and PP-HMDSZ films obtained at different discharge frequencies are shown in Figs. 7 and 8, respectively; in producing these films, plasma parameters other than frequency were chosen as similar as possible. Figure 9 represents the IR spectra of 2.45 GHz PP-HMDSO films produced at different power densities (A, 0.6 W/cm^3; B, 2.5 W/cm^3).

Referring to Fig. 7, one may note numerous spectral features which the polymer films have in common with HMDSO monomer:

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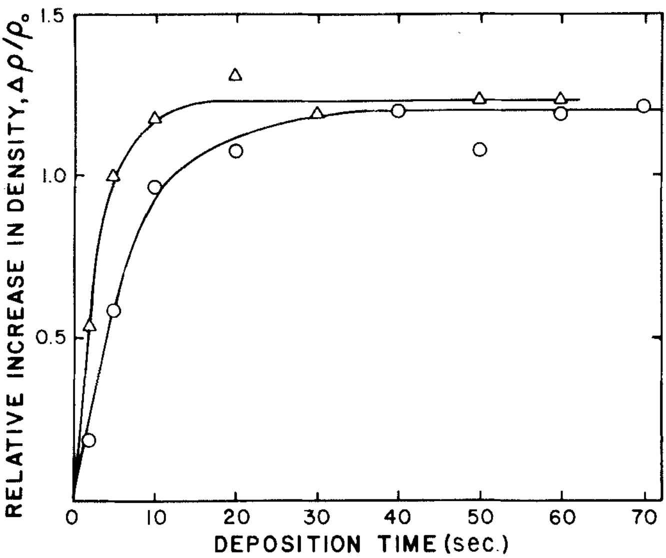

FIG. 6. Relative increase in density for (○) PP-HMDSO and (△) PP-HMDSZ films as a function deposition time.

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these include the absorption bands at 1100 - 1000 cm^{-1}, corresponding to ν_{as} (Si–O–Si) vibration [14], at 1250 cm^{-1}, attributed to $\delta_s(CH_3)$ vibrations in methylsilyl groups, and at 840 cm^{-1}, attributed to ν(Si–C) vibrations in $Si(CH_3)_3$ groups. In addition, the polymer spectra exhibit bands which are absent from the monomer spectrum: that at 2120 cm^{-1} corresponds to ν(SiH) vibration, and that at 800 cm^{-1} (see Fig. 7, A-C) is attributed to ν(Si–C) and $\rho(CH_3)$ vibrations in $Si(CH_3)_2$ groups. These latter groups may form by monomer fragmentation via abstraction of methyls from silicon and of hydrogen from methyl groups.

Comparing the various spectra in Fig. 7, one may also note qualitative changes in some absorption bands with increasing discharge frequency: for example, a distinct broadening of the 1100-1000 cm^{-1} band points to an increase in the concentration of Si–O bonds in the polymer structure. The wide absorption band between 850 and 750 cm^{-1} for the 2.45 GHz film (Fig. 7D) arises from overlapping of absorptions due to ν(Si–C) and $\rho(CH_3)$ vibrations in methylsilyl groups with differing numbers of methyl substituents attached to the Si atom [14]. In the present case these substituents are presumably formed by differing fragmentations of $Si(CH_3)_3$ groups in the microwave discharge.

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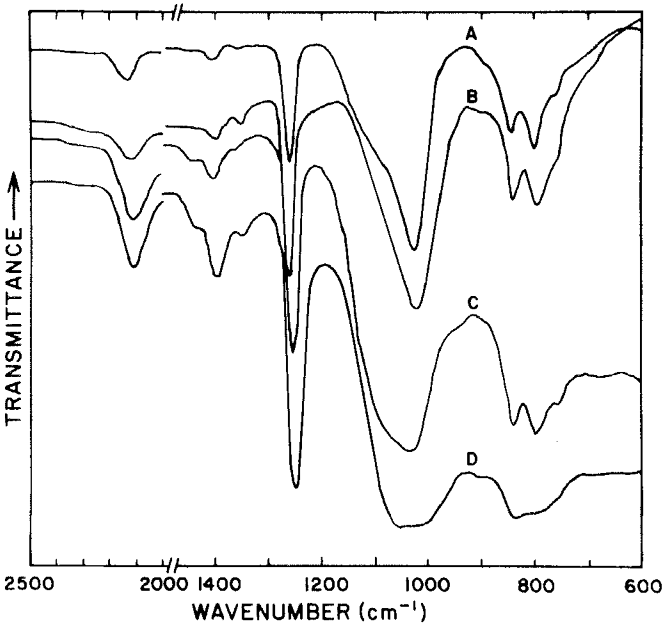

FIG. 7. Infrared spectra of PP-HMDSO films deposited at various discharge frequencies for various polymerization conditions and IR reflection techniques: (A) 2 kHz, 0.04 W/cm^3, 0.3 Torr, ATR; (B) 20 kHz, 0.2 W/cm^3, 0.2 Torr, ATR; (C) 5 MHz, 0.1 W/cm^3, 0.2 Torr, MIR; (D) 2.45 GHz, 0.6 W/cm^3, 0.2 Torr, MIR.

Turning now to the IR spectra of PP-HMDSZ, shown in Fig. 8, we note that several bands already discussed in connection with PP-HMDSO are also present here, for example, at 2120, 1250, and 840 cm^{-1}. Considering the 20 kHz spectrum (Fig. 8A), one can further identify absorption bands at 1170 and 920 cm^{-1} which are characteristic for the Si-NH-Si system, corresponding to δ(NH) and ν_{as}(Si-N-Si) vibrations, respectively [14]. A new band, absent from the monomer spectrum, may also be noted at 1020 cm^{-1}; this band corresponds to $\omega(CH_2)$ vibration, and points to the presence of methylene and ethylene linkages between Si atoms. This, in turn, is indicative of crosslinking in the polymer, resulting from the abstraction of hydrogen atoms and of methyl groups.

The spectra of Fig. 8 show a marked decrease in the intensity of the $Si(CH_3)_3$ band at 840 cm^{-1} with increasing discharge frequency, and also the formation of a broad band between 950 and 750 cm^{-1} (Fig. 8D) in the case of the 2.45 GHz polymer film. This latter band is due to

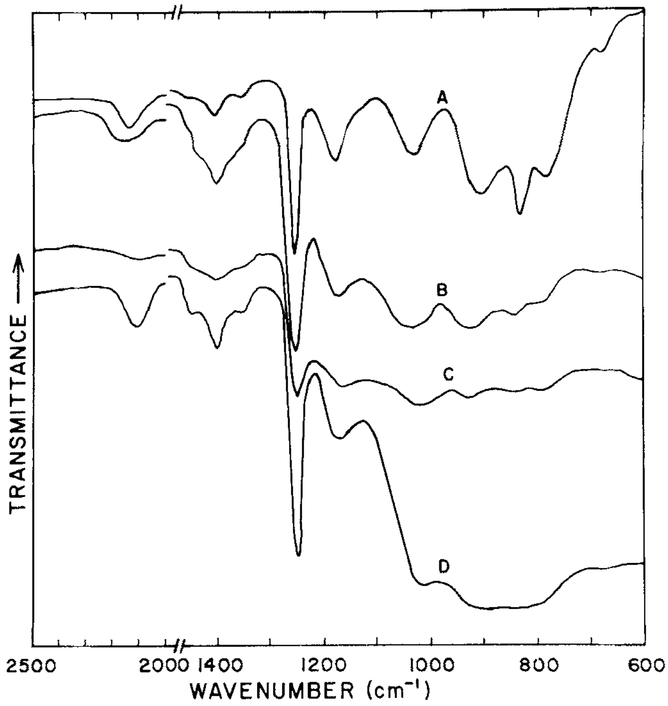

FIG. 8. Infrared spectra of PP-HMDSZ films deposited at various discharge frequencies for various polymerization conditions and IR reflection techniques: (A) 20 kHz, 0.2 W/cm^3, 0.2 Torr, ATR; (B) 5 MHz, 0.1 W/cm^3, 0.2 Torr, MIR; (C) 5 MHz, 0.7 W/cm^3, 0.2 Torr, MIR; (D) 2.45 GHz, 0.6 W/cm^3, 0.2 Torr, MIR.

an overlap of absorptions in this spectral region which presumably result from an increasing concentration of Si-N bonds in the structure of this particular polymer.

Finally, comparing spectra A (the same as Fig. 7D) and B of Fig. 9, we note the features already discussed in connection with Fig. 7, except that for Fig. 9B the 1250 cm^{-1} (methyl vibration) band is proportionately much less intense than the 1100-1000 cm^{-1} Si–O band, for example. This is presumably due to more extensive fragmentation at the higher power density.

The infrared results will be discussed further in the next section.

DISCUSSION

It is generally accepted that plasma polymers differ from their "conventional" counterparts both by the presence of some different

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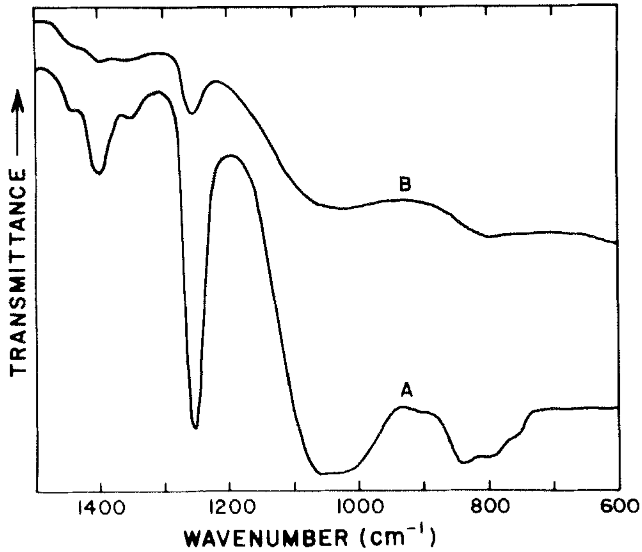

FIG. 9. Infrared spectra of PP-HMDSO deposited at different power densities in 2.45 GHz discharges: (A) 0.6 W/cm^3; (B) 2.5 W/cm^3.

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structural groups, as well as by a higher degree of crosslinking. The results of the present work amply substantiate this view and, in addition, show that plasma characteristics, in particular the discharge frequency, can significantly affect the structure of a plasma polymer film. Results of density measurements in the present work, further, reveal a possible mechanism which could explain some of these observations.

With respect, firstly, to the structure of our polymer films, evidence for crosslinking may be found both in the density data, as well as in the infrared spectra: the high plateau densities (~ 1.7 g/cm^3) of the present 2.45 GHz plasma polymers are indicative of extensive crosslinking and of a considerable amount of inorganic structure, as discussed in greater detail below. This, in turn, suggests that a particularly high degree of fragmentation of monomer molecules takes place in the microwave discharge, for it is the reactive (radical) species created in the plasma which are primarily responsible for formation and crosslinking of the film. In the case of HMDSO and HMDSZ monomers, which contain no olefinic double bonds, radical species result from the abstraction of hydrogen, methyl- or other substituent groups in the plasma; the high p_d/p_0 values of close to 2 under the plasma conditions of this work bear witness to the extensive fragmentation in the microwave discharge.

For comparison, Yasuda [15] obtained a value for p_d/p_0 of 1.50 for HMDSO in a radiofrequency (13.56 MHz) discharge, but this may be due in part to the different experimental conditions (plasma parameters, reactor geometry, pumping rate, etc.). Unfortunately, p_d/p_0 could not be measured in the present radiofrequency experiments, but the implied correlation between discharge frequency, extent of fragmentation and plasma polymer density appear to be well borne out by the lower (1.16 g/cm^3) density of our 5 MHz PP-HMDSO films.

The strong fragmentation and resulting high crosslink density are also reflected by the infrared data: from Figs. 7 and 8, Si–O and Si–N bond concentrations in PP-HMDSO and PP-HMDSZ, respectively, are seen to be substantially higher in the 2.45 GHz films than in films produced in the lower frequency discharges. The broadening of the corresponding absorption bands and the "smearing-out" of structural features (for example, near 1000 and 800 cm^{-1} in Fig. 7, and between 950 and 750 cm^{-1} in Fig. 8) further indicate the increased inorganic structure and cross-linking in these films, as already discussed; this is compatible with the high density of these films. Power density in the plasma appears to affect the IR spectra to a lesser extent, as may be inferred from a comparison of the spectra of Figs. 8B, C and D. Nevertheless, a large increase in power density (at the same discharge frequency) evidently gives rise to more extensive fragmentation, hence more inorganic structure, as illustrated by the spectra of Fig. 9 for 2.45 GHz films.

Considering the density-deposition time curves (Figs. 4 and 5) in the light of the above, we note that there is ample reason for confidence in the density data: their reproducibility has been excellent for both monomers, and for deposits on the different substrates. Confidence in the initial (sloping) portion of the curves is additionally enhanced by the fact that the backward extrapolation to the ordinate axis exactly yields the liquid monomer density. The higher densities of the plasma polymers are not entirely surprising: Knickmeyer et al. [16] have reported densities of nine different radiofrequency plasma polymers (no organosilicones), measured in a density gradient column. The plasma polymers were found to be up to 30% denser than their conventional counterparts. The result for the present 5 MHz PP-HMDSO film (~ 20%) is comparable, though the densities of the 2.45 GHz films are, of course, substantially higher. What is, however, quite surprising with regard to the present density data is the shape of the curves in Figs. 4 and 5; these have numerous implications: (1) For the case of very thin films ($t \lesssim 10$ s) the density (and consequently, the structure) are liquid-like and strongly depend upon t. (2) For the case of thicker films ($t \gg 10$ s) one may postulate a heterogeneous structure (i. e., a "density profile") consisting of a dense, solid bulk (adjacent to the substrate), and a liquid- or oligomer-like outer layer (the last to have been deposited). In fact, one can recast the data in Figs. 4 and 5 in order to expand upon this argument: in these figures, ρ is the average density of the existing deposit, from

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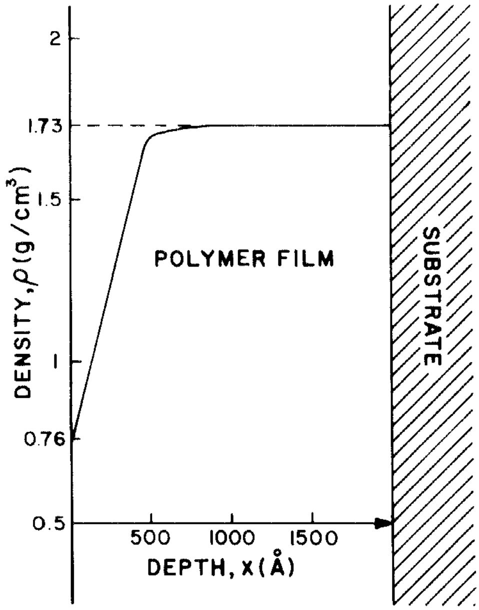

FIG. 10. Profile of local polymer density $\rho(x)$ versus depth x of PP-HMDSO.

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which a local density value, $\rho(x)$, can be calculated (x being the depth of deposit) from the relationship $\rho(x) = dW(x)/dx$, where W(x) is the weight per unit area of polymer deposited. This has been done for PP-HMDSO in Fig. 10: the first ~ 500 Å layer from the film surface is "oligomeric", the remainder a dense, highly crosslinked solid with $\rho_{sol} = 1.73$ g/cm^3. We emphasize that this profile is semiquantitative and that the method used here is obviously neither capable of revealing any possible substructure in the "oligomeric" surface layer nor, for that matter, its precise thickness. Figures 5 and 6 have shown steeper rises for PP-HMDSZ than for PP-HMDSO, implying a thinner "oligomeric" layer. This appears to be due to structural differences between the two monomers: HMDSZ presumably crosslinks more readily than HMDSO via abstraction of hydrogen from –NH– groups and formation of bonds between Si atoms via tertiary nitrogen [17].

Now, since the "solid" portion of the profile must have been "oligomeric" initially, we conclude that a relatively slow (of the order of seconds) transformation process is active which proceeds appreciably only in the plasma environment. We suggest further that the transformation from oligomer to solid involves a combination of at least two processes: diffusion of free radical species in the solid state, followed by recombination (crosslinking) reactions; and photochemically induced crosslinking reactions, in particular those involving energetic (UV) photons. Such reactions are known to occur even in micron-thick films [18].

Finally, we reemphasize that the dense solid constituent of the film is quite unlike its conventional counterpart, having been seen to have a very high "inorganic" content. A rough proportion of inorganic/organic structure content may be calculated by applying a linear mixing relationship to the density data, by using the values for polymethylsiloxane (PMS, $\rho = 0.98$ g/cm^3) and vitreous silica (VS, $\rho = 2.20$ g/cm^3) as the two extremes. This shows that the volumetric ratio

$$\phi_{VS}/\phi_{PMS} = 1.60 \tag{1}$$

that is, PP-HMDSO more closely resembles vitreous silica than polymethylsiloxane. In the case of PP-HMDSZ ($\rho = 1.75$ g/cm^3) this ratio is somewhat less, as amorphous Si_3N_4 is rather dense ($\rho = 3.4$ g/cm^3).

As a final comment, the results presented here strongly suggest the possibility of controlling composition and morphology of plasma polymer films. This should be highly desirable from the point of view of the various applications mentioned earlier. Present evidence suggests that this may be accomplished by controlling plasma conditions, in particular the discharge frequency, and the power density in the plasma. Other approaches are presently under investigation in this laboratory.

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CONCLUSIONS

Plasma polymerization of hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSZ) monomers has been carried out in audio- (2 kHz, 20 kHz), radio- (5 MHz), but principally in microwave (2.45 GHz) frequency discharges. In the latter case an LMP apparatus has been used.

Film growth kinetics on glass and aluminum substrates have been studied by thickness and gravimetric measurements. These complementary data have led to precise determinations of the film densities which, in turn, provide strong evidence for a hitherto unreported structural feature: the present organosilicon films appear to be composed of a dense, highly crosslinked solid phase, and a thin (several hundred angstroms thick) "oligomeric" surface layer. The solid component is about 70% denser than the equivalent "conventional" polymer and has a marked inorganic character; for example, in the case of PP-HMDSO the ratio of the inorganic (amorphous silicalike) to organic ("conventional" polymethylsiloxanelike) structural contents has been estimated at 1.6.

Infrared spectroscopic analyses of polymers produced in lower frequency discharges tend to show narrow, well resolved absorption bands. In the case of 2.45 GHz films, on the other hand, bands corresponding to inorganic linkages (Si–O, Si–N, Si–C) tend to become broader and more intense, and structural features become smeared-out. This is indicative of crosslinking and of the increased inorganic structural content referred to above. The same trend towards increasing inorganic structure is noted, at a given discharge frequency, when films are produced at high power density in the plasma.

These results indicate a particularly intense fragmentation of monomer molecules in the microwave plasma, as substantiated by pressure-rise measurements. Radical species created by abstraction of hydrogen, methyl- or other groups then give rise to film formation and growth, and to cross-linking reactions within the film. The latter may be enhanced by ultraviolet irradiation in the plasma environment.

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