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Polymerization of Organosilicones in Microwave Discharges. II. Heated Substrates

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ABSTRACT

Organosilicone vapors [hexamethyldisiloxane (HMDSO), hexamethyldisilazane (HMDSN), and hexamethylcyclotrisilazane (HMCTSN)] have been polymerized in a microwave plasma. The reaction kinetics, structure, and density of the plasma polymer films were studied as a function of substrate temperature (T_s) to 800°C, using metal or glass as the substrate.

Deposition rates for both HMDSO and HMDSN decrease with substrate temperature from near 80 Å sec⁻¹ on an unheated substrate to about 30 Å sec⁻¹ above 400°C. The densities of plasma polymers, already high (~1.7 g/cm³) compared with conventional organosilicone polymers (~1.0 g/cm³) when $T_s = 25^\circ\text{C}$,

increase further with increasing substrate temperature. These high densities (near 1.9 g/cm³) indicate that for T_s above ~500°C, little "organic" content remains in the plasma polymers. Infra-red spectra of plasma polymerized HMDSO, HMDSN, and HMCTSN

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show that these materials differ structurally from their more familiar counterparts, confirm the increasing importance of inorganic linkages at rising T_g , and support the concept that the plasma polymers are intensely cross-linked. The great complexity of plasma polymerization reactions is further documented by the reported results.

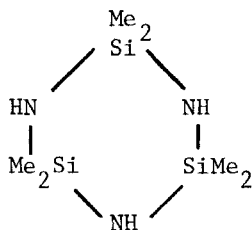
INTRODUCTION

In previous papers [1, 2] it has been shown that the chemical structure and properties of thin, plasma-polymerized organosilicone films can be modified by appropriate thermal treatments following polymerization. Heat treatment reduced the organic content of such films, correspondingly increasing their inorganic character. Thermally modified organosilicone films were found to be unusually interesting, displaying high temperature stability, strong adhesion to metal substrates, and high resistance to corrosive fluids, thus promising useful applications; for example, as coatings for the passivation of metals [3].

The earlier work suggested combining thermal modification and polymerization steps during the actual exposure of substrates to plasmas. This concept offers the advantage of more closely controlling the properties to be built into the plasma polymer through combined control of reaction parameters, notably substrate temperature, and the physical variables of plasma generation (pressure, power density, monomer feed rate, etc.).

Accordingly, the present paper reports the results of a study on the deposition kinetics, chemical structure, and density of thin films deposited on heated substrates by microwave plasma polymerization of organosilicone monomers: (1) hexamethyldisiloxane (HMDSO), (2) hexamethyldisilazane (HMDSN), and (3) hexamethylcyclotrisilazane (HMCTSN), the chemical structures of these being as follows:

- (1) $\text{Me}_3\text{Si}-\text{O}-\text{SiMe}_3$; (2) $\text{Me}_3\text{Si}-\text{NH}-\text{SiMe}_3$; (3)



The use of microwave frequency for plasma polymerization is advantageous because the electron density of microwave discharges

is higher than that at lower frequencies. Consequently, a higher degree of monomer fragmentation can be achieved which, in turn, leads to the formation of highly cross-linked structures in the polymer films. Indeed, recent results [4] have shown that films produced from HMDSO and HMDSN in microwave frequency discharges are characterized by higher densities (resulting from high inorganic content and cross-linking) than those deposited in audio- or radio-frequency discharges. The use of microwave plasmas for the deposition of films on heated substrates seemed to be indicated, particularly for the production of plasma-polymer films with low concentrations of organic groups.

EXPERIMENTAL

The large volume microwave plasma generator (LMP), operating at 2.45 GHz and used in this work, has been described previously [5, 6]. Plasmas were generated in a modified reactor system, shown schematically in Fig. 1. The reactor consists of a quartz tube with a side sleeve for incorporating the heated substrate. Films were deposited either directly on a $5\text{ cm} \times 3\text{ cm} \times 50\text{ }\mu\text{m}$ stainless steel foil fixed between two brass holding rods, or onto glass flats in

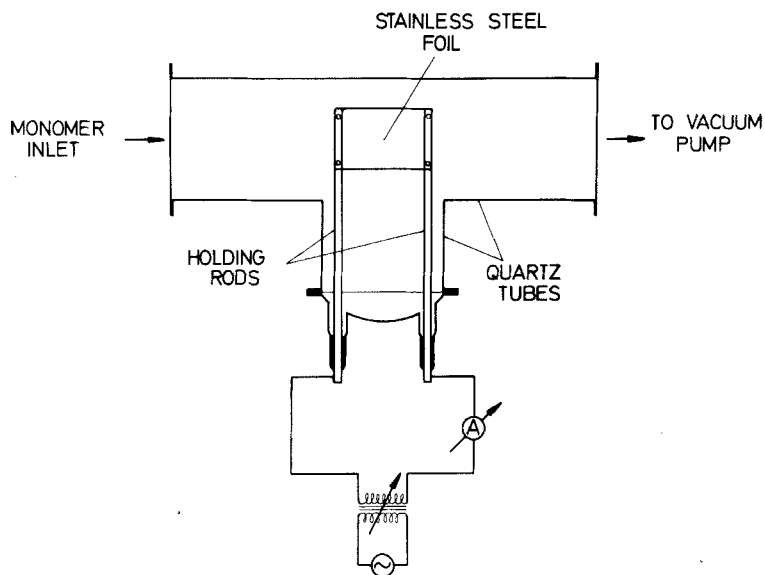


FIG. 1. Reactor system with heated substrate.

good thermal contact with the foil. The foil was heated by an electrical current (10 to 45 A), supplied through the holding rods. Calibration of substrate temperature versus heating current was carried out in vacuum (0.4 torr) by observing known melting points of suitable substances placed on the substrate surface. This calibration employed material standards offered commercially as Tempilstiks (Tempil Division, Big Three Industries, Inc. South Plainfield, New Jersey).

Prior to polymerization, the reactor pressure was reduced to $\approx 10^{-3}$ torr (using a 2-stage mechanical pump, Leybold Heraeus, Model D30A); following this the monomer vapor was introduced continuously through a needle valve, from a calibrated reservoir, maintaining a steady, dynamic pressure of 0.2 torr and a liquid monomer flow rate of $0.05 \text{ cm}^3/\text{min}$. The pressure in the reactor was measured using a capacitive pressure gauge (MKS Baratron, Type 170M). Stable microwave discharges were obtained with a power density in the plasma of 0.3 W/cm^3 . Polymerizations were carried out at substrate temperatures of 25, 200, 400, 600, and 800°C . The elevated temperatures were controlled to better than $\pm 10^\circ\text{C}$. Deposition kinetics (weight of film per unit area and film thickness, both as functions of duration of deposition under a given set of experimental conditions) were measured using the procedures described earlier [4]: film thicknesses were determined interferometrically using a Sloan Angstrometer (Model M-200), and weights of deposits were determined with a Sartorius Model 2600 electronic digital microbalance. The combination of these two data sources permitted calculation of polymer densities, as described in Ref. 4. Infrared spectra of polymer films deposited on stainless steel foils were recorded on a Perkin-Elmer Model 467 spectrophotometer using the attenuated total reflection (ATR) method. Spectral grade HMDSO, HMDSN, and HMCTSN (PCR Research Chemicals, Inc.) monomers were used without further purification.

RESULTS AND DISCUSSION

Deposition Kinetics and Film Densities

In Ref. 4 we reported the deposition kinetics of plasma polymerized HMDSO (PP-HMDSO) and of PP-HMDSN onto unheated substrates. It was shown that, for a given choice of deposition parameters (pressure, power density in the plasma, monomer flow rate), plots of deposit thickness and of weight of deposit per unit area versus duration of deposition were virtually linear except for slight deviations explained in Ref. 4. On this basis, then, it is justifiable to speak of a "deposition rate" (either in $\text{\AA}/\text{sec}$ or in $\mu\text{g cm}^{-2} \text{ sec}^{-1}$, as the case may be), provided the other deposition parameters are specified. Deposition rates were found to be essentially the same for the

substrate materials investigated (glass, aluminum). It was also shown that the independent gravimetric and thickness measurements can be combined to yield accurate values of the average density of the deposit, and these density data revealed that the plasma polymer films consist of a very dense "solid" layer and a thin (~ 500 Å thick) "oligomeric" surface layer. (The existence of this heterogeneous film structure and the transformation mechanism from "oligomer" to "solid" proposed in Ref. 4 are the subject of further experiments, to be discussed elsewhere.)

In this section we present deposition rate and density data which have been obtained at elevated substrate temperatures, T_s . The other deposition parameters were kept constant, namely: pressure = 0.2 torr, power density in the plasma ≈ 0.4 W/cm³, and monomer flow rate ≈ 0.06 cm³/min. Thickness and weight per unit area of films deposited onto glass substrates (Corning cover glass No. 1) were determined for at least six deposition durations ranging from 40 sec to 5 min at a given value of T_s . It is noteworthy that these curves were rigorously linear for $T_s \geq 200^\circ\text{C}$, suggesting that the "oligomer" layer is either absent or much thinner under these conditions.

Figures 2 and 3 show deposition rates (in Å/sec and in $\mu\text{g cm}^{-2} \text{sec}^{-1}$, respectively) as a function of T_s (ranging from 25 to $\sim 500^\circ\text{C}$),

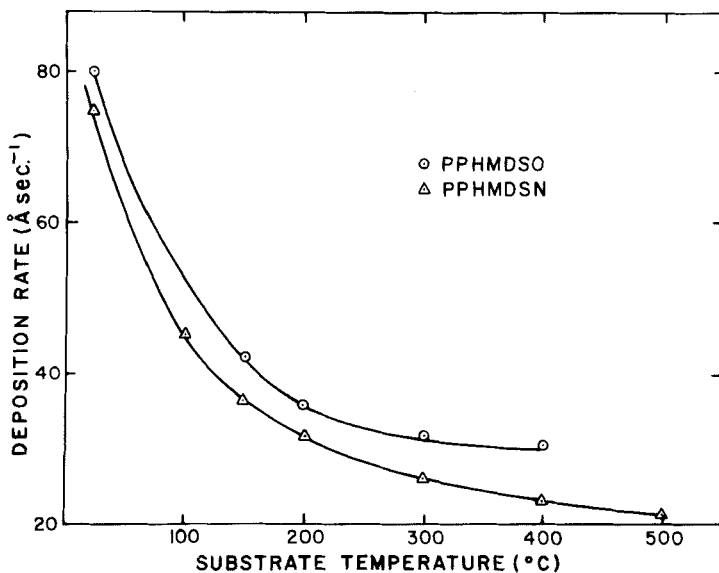


FIG. 2. Deposition rates of PP-HMDSO and PP-HMDSN: film thickness data.

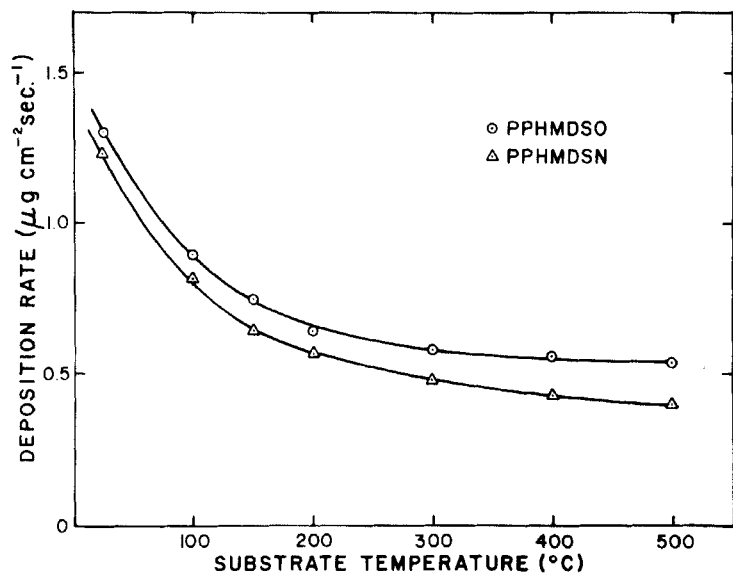


FIG. 3. Deposition rates of PP-HMDSO and PP-HMDSN: gravimetric data.

for both PP-HMDSO and PP-HMDSN. The deposition rate drops sharply between 25 and about 200°C, then more gradually, and the behavior is seen to be qualitatively similar for the two monomers investigated. Quantitatively, the deposition rates are about 50% higher in the case of PP-HMDSO in the range $300^{\circ}\text{C} \lesssim T_s \lesssim 500^{\circ}\text{C}$, and they are almost constant while the values for PP-HMDSN are still decreasing. The reasons for this are not known at present, but may be linked with more complex, multiple cross-linking mechanisms in the case of the latter monomer.

Again, in accord with previously described procedures [4], we have calculated the film densities, ρ , and the results are shown in Fig. 4 as a function of T_s . This figure shows very clearly that the already high ρ values of about 1.7 g/cm³ increase even further as T_s is increased beyond 25°C, attaining values approaching 1.9 g/cm³ for $T_s = 500^{\circ}\text{C}$. As was already pointed out in Ref. 4, PP-HMDSO and PP-HMDSN are much denser than "conventional" polymers, and thus more closely resemble vitreous silica ($\rho = 2.2$ g/cm³) and amorphous silicon nitride ($\rho = 3.4$ g/cm³), respectively. (For comparison, the density of "conventional" polymethylsiloxane is 0.98 g/cm³.) Figure 4 shows that this resemblance is even further enhanced by high T_s .

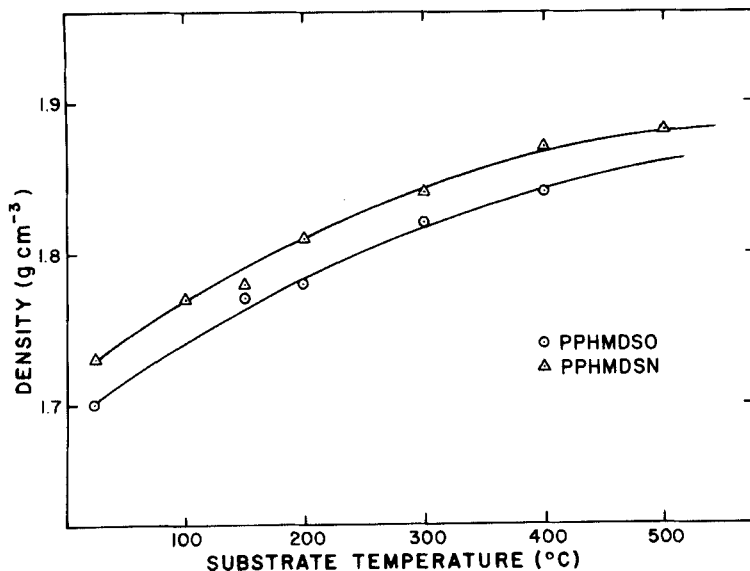


FIG. 4. Variation of density of plasma-polymerized organosilicone polymers as a function of substrate temperature.

values: on the basis of film density, one would expect plasma polymers prepared at $T_s \gtrsim 500^\circ\text{C}$ to have very little "organic" structural content. This is, indeed, borne out by infrared spectra, presented in the next section. The density (and infrared) data further show that the degree of inorganic structure can be controlled by simply choosing the appropriate T_s value.

Finally, the important structural and physicochemical variations produced by changing T_s in the plasma polymerization of HMDSO, HMDSN, and HMCTSN were confirmed by qualitative tests of film hardness and of their ability to passivate the metal substrates to aggressive environments. Scratch and abrasion tests showed a progressive hardening of the plasma polymer films as T_s increased.

Films deposited at substrate temperatures of 800°C were found to be colorless, glassy materials which adhered tenaciously to the substrates, and from which they could not be removed without destroying the metal substrate. These latter films also showed outstanding resistance to acids and bases over a broad range of temperatures. These trends are in keeping with the density (and infrared) analyses, notably with the predominance of inorganic structure and with the augmented cross-link density of films produced at elevated T_s .

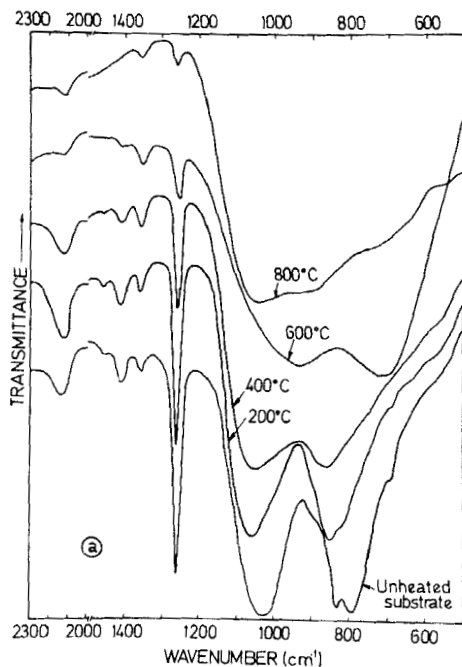


FIG. 5a. Infrared ATR spectra of polymer films deposited at various substrate temperatures from HMDSO.

Infrared Spectra

The effects of substrate temperature, T_s , on the structure of plasma polymer films deposited on stainless steel substrates were documented by IR spectra. The spectra of films obtained from HMDSO, HMDSN, and HMCTSN are given as Figs. 5a, 5b, and 5c, respectively. In the spectra of films deposited onto unheated substrates (reference condition), several common absorption bands are noted, and may be assigned to hydrogen- and carbon-containing silyl groups:

1. 2120 cm^{-1} , broad band assigned to $\nu(\text{SiH})$ vibration [7]
2. 1410 cm^{-1} , corresponding to $\delta_{as}(\text{CH}_3)$ vibrations of methyl groups attached to silicon atoms
3. 1360 cm^{-1} , weak but distinctive band characteristic of $\delta_s(\text{CH}_2)$ vibration in $\text{Si-CH}_2\text{-Si}$ groups
4. 1260 cm^{-1} , sharp and very intense band attributed to $\delta_s(\text{CH}_3)$ vibration of methyl groups on silicon atoms

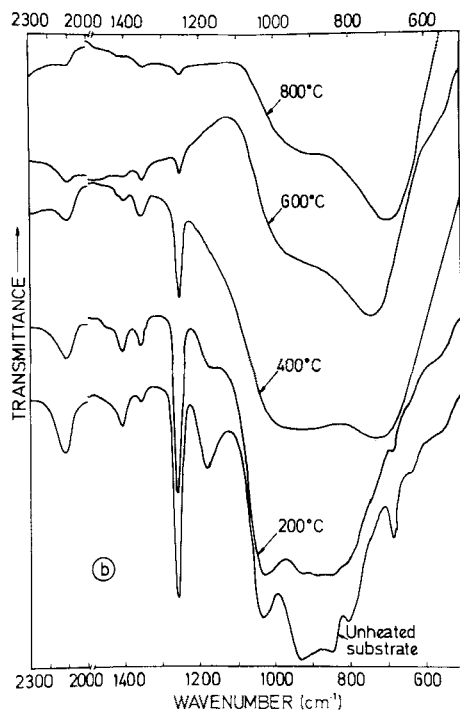


FIG. 5b. Infrared ATR spectra of polymer films deposited at various substrate temperatures from HMDSN.

5. 1030 cm^{-1} , corresponding to $\omega(\text{CH}_2)$ vibration in $\text{Si}-(\text{CH}_2)_1$ or 2 $-\text{Si}$ groups

This latter band is only seen in the spectra of PP-HMDSN and PP-HMCTSN (Figs. 5b and 5c) and cannot be detected in the spectrum of PP-HMDSO (Fig. 5a), due to overlap with the Si-O-Si band also appearing in this region; finally, we observe

6. $870\text{--}750\text{ cm}^{-1}$, attributed to $\nu(\text{SiC})$ and $\rho(\text{CH}_3)$ vibrations in methylsilyl groups with different numbers of methyl substituents

The polymer spectra also exhibit bands which originate from the characteristic structural units in particular monomers. Thus the spectrum of PP-HMDSO (Fig. 5a) shows a very strong band in the region of $1100\text{--}1000\text{ cm}^{-1}$ corresponding to $\nu_{\text{as}}(\text{Si-O-Si})$ vibration. In the spectra of PP-HMDSN and PP-HMCTSN (Figs. 5b and 5c),

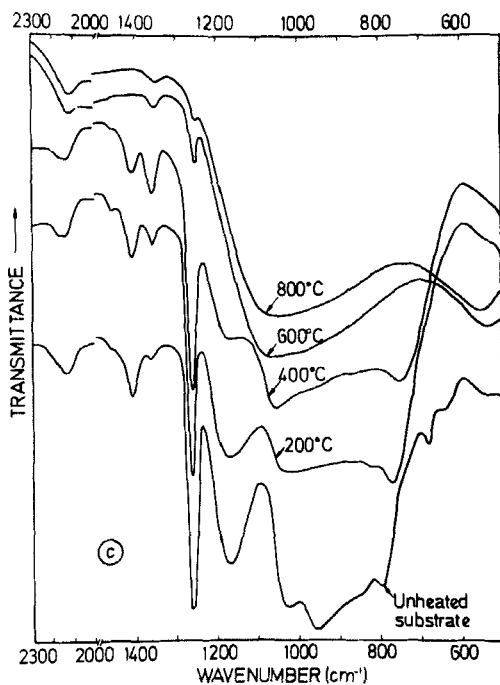


FIG. 5c. Infrared ATR spectra of polymer films deposited at various substrate temperatures from HMCTSN.

one can identify absorption bands at 1170 cm^{-1} and $950\text{--}930\text{ cm}^{-1}$ which are characteristic of Si-NH-Si systems, and correspond to $\delta(\text{NH})$ and $\nu_{\text{as}}(\text{Si-N-Si})$ vibrations, respectively [7].

It should be noted that absorption bands (1), (3), and (5) (Figs. 5a, 5b, and 5c), which represent SiH and Si-(CH₂)₁ or ₂-Si groups, respectively, are not observed in the corresponding spectra of monomers. Formation of these groups in the polymer structure results from the fragmentation of monomers under plasma conditions by hydrogen, and methyl abstraction from methyl-silyl groups [8]. A simplified scheme for the process is as follows:



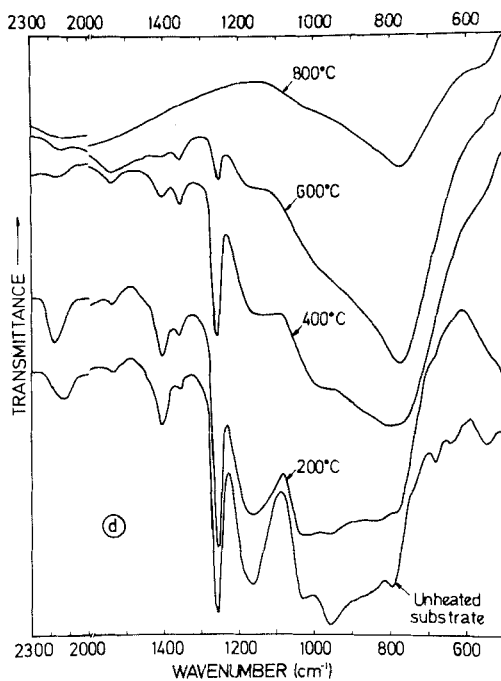
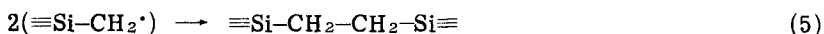
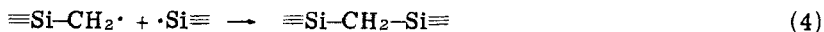


FIG. 5d. Infrared ATR spectra of polymer films deposited at various substrate temperatures from HMCTSN and ammonia.



Reactions (4) and (5) involve cross-linking of the polymer film. In the IR spectra of Fig. 5a, Band c shows the strong dependence of plasma polymer film structure on substrate temperature, T_s ; a corresponding influence of T_s on ρ was discussed in the preceding section. The absorption bands at 2120 (SiH), 1410, and 1260 cm^{-1} (SiCH₃) decay markedly with increasing T_s , presumably due to thermal scission of Si-H and Si-C bonds during film growth. The increased absorption at 1360 cm^{-1} (Si-CH₂-Si), also noted with increasing T_s , is thought to be due to cross-linking of the polymer through the formation of methylene linkages between silicon atoms. This takes place via Reactions (1), (2), and (4), and the reaction is initiated thermally.

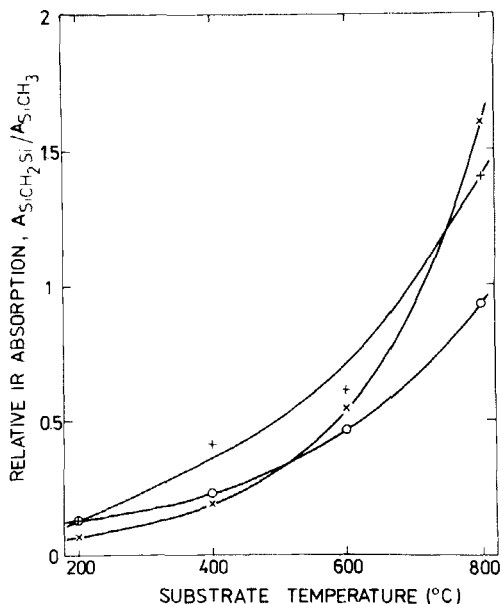


FIG. 6. Relative intensity of IR absorption $A_{\text{SiCH}_2\text{Si}}/A_{\text{SiCH}_3}$ as a function of substrate temperature for (○) PP-HMDSO, (+) PP-HMDSN, and (×) PP-HMCTSN.

In order to study this process more precisely, relative changes of absorption intensity at 1360 and 1260 cm^{-1} , corresponding to $\delta_s(\text{CH}_2)$ vibration in $\text{Si}-\text{CH}_2-\text{Si}$ and $\delta_s(\text{CH}_3)$ vibration in methylsilyl groups, respectively, were examined as a function of substrate temperature. Absorption data were expressed as the ratio $A_{\text{SiCH}_2\text{Si}}/A_{\text{SiCH}_3}$, these being the peak areas at 1360 and 1260 cm^{-1} , respectively. This ratio is shown plotted as a function of T_s in Fig. 6, and it shows an increase in the relative concentration of $\text{Si}-\text{CH}_2-\text{Si}$ groups in the structure of polymer films. The higher values of this ratio, noted for films deposited from the organosilazane monomers at 800°C , may result from a higher degree of methyl abstraction from methylsilyl groups, presumably due to structural differences between the silazane and siloxane monomers. The organosilazanes appear to cross-link more readily than organosiloxanes, producing not only $\text{Si}-\text{CH}_2-\text{Si}$ linkages, but cross-linking also via abstraction of hydrogen from $-\text{NH}-$ groups and by the formation of Si radicals from the scission of $\text{Si}-\text{C}$ (Reaction 1) and of $\text{Si}-\text{N}$ bonds in reactions with tertiary nitrogen [2, 4, 9]. This result would point to relatively higher densities in the silazane

polymers, as was indeed observed (see the preceding section). With further reference to Figs. 5a, 5b, and 5c, significant qualitative changes in the absorption bands at lower wave numbers—notably 1200–600 cm^{-1} —occur at increasing substrate temperatures. Evidently higher T_s values result in broad, asymmetric bands in the spectra of the corresponding plasma polymer films. These are characteristic of inorganic silicone compounds. The asymmetry of these bands reflects a strong overlapping effect of absorption in this region. Infrared data consequently cannot provide detailed information about the structure of the present films deposited at temperatures above about 400°C. This limitation must be considered specific to the present choice of monomers and substrate, at least for the time being.

The spectra of PP-HMDSO (Fig. 5a) show a rise in the Si–O–Si absorption band in the region 1100–1000 cm^{-1} with increasing T_s . A distinct shift in the SiCH₃ absorption band at 850–750 cm^{-1} toward higher wave numbers is also observed, and this is presumably due to the formation of inorganic silicon-carbon linkages. It can be seen from the 800°C spectrum that this band, appearing in the 950–850 cm^{-1} region, is strongly interfered with by the Si–O band at 1100–1000 cm^{-1} . Some irregularity at $T_s = 600^\circ\text{C}$ is acknowledged, as the corresponding spectrum (Fig. 5a) is clearly different from the other spectra, showing two absorption bands at 1000–900 and 800–650 cm^{-1} . This irregularity in the polymer structure gives evidence for the very complex reaction chemistry of the plasma process, and for the additional complication introduced by the substrate temperature effect. The entire subject warrants continued investigation.

The spectra of PP-HMDSN and PP-HMCTSN (Figs. 5b and c) show characteristic absorption bands at 1170 cm^{-1} , corresponding to –NH– groups in Si–NH–Si structures, which decay with increasing substrate temperature. We suggest that thermal scission of N–H bonds and cross-linking via the formation of Si–N linkages [2] take place. The increase of substrate temperature to 800°C gives rise to the appearance of broad and asymmetric bands in the regions 1100–600 cm^{-1} for PP-HMDSN (Fig. 5b) and 1200–800 cm^{-1} for PP-HMCTSN (Fig. 5c). Again asymmetry here may result from the overlapping of absorption bands corresponding to Si–N and Si–C inorganic linkages, both contained in the structure of polymers due to thermal decomposition processes.

Earlier studies [1, 2] have shown that the addition of ammonia to HMCTSN vapor produces cross-linking in the plasma polymer film through the formation of Si–NH–Si linkages, and that the films so produced have increased thermal stability and strong adhesion to metal substrates. In the present work we have included a study of the effect of substrate temperature on the structure of PP-organosilazanes. Plasma polymerization was carried out from mixtures of HMCTSN and NH₃ vapors, each at a partial pressure of 0.1 torr, all other discharge parameters being maintained at the levels specified above.

The IR spectra of polymer films deposited from this mixture are given in Fig. 5d.

In general, the changes in the absorption bands (i), (ii), (iii), and (iv) with increasing T_s follow trends analogous to those noted for the spectra in Figs. 5a, 5b, and 5c. In addition, the absorption at 1170 cm^{-1} ($-\text{NH}-$ groups) decreases more slowly with increasing T_s than in the case of polymer deposited without ammonia (Fig. 5c). Complete decay of this band is noted only at 800°C , whereas for polymer deposited without ammonia (Fig. 5c) the decay occurs at or below 600°C . Presumably, this is again due to the higher concentration of $\text{Si}-\text{NH}-\text{Si}$ bonds in the polymer film deposited in the presence of ammonia [1, 2]. The reactivity of ammonia with HMCTSN monomer is also indicated by the appearance in Fig. 5d of a new absorption band at 1540 cm^{-1} , attributed to $\delta_s(\text{NH}_2)$ vibration in $\text{Si}-\text{NH}_2$ groups [7]. The effect of ammonia on polymer structure is also manifested by the different responses to substrate temperatures as seen in the spectra of Figs. 5d and 5c: a broad, intense absorption band with a sharp maximum near 800 cm^{-1} appears in the spectrum of polymer film deposited at 800°C (Fig. 5d), and this is similar to a band observed in the spectrum of silicon nitride [10-12]. Evidently, plasma-initiated reactions of ammonia and monomer lead to increased concentrations of $\text{Si}-\text{NH}-\text{Si}$ linkages in the polymer [1], which then responds to thermal decomposition reactions to form $\text{Si}-\text{N}$ inorganic bonds with tertiary nitrogen [2].

To confirm this interpretation, the effect of oxygen on the polymer structure was also examined. Figure 7, Curve B, shows the IR spectrum of polymer film deposited from the mixture of HMCTSN vapor and oxygen at $T_s = 800^\circ\text{C}$, all other polymerization conditions being as in previous experiments. Figure 7 also reproduces, for comparison, the spectra of polymer films deposited from pure HMDTSN (Curve A) and from the mixture with ammonia (Curve C), both at the same substrate temperature. These spectra show quite remarkable qualitative changes in plasma polymer film structure arising from the admixture of reactive gases to the HMCTSN. The presence of oxygen leads to the appearance of an intense absorption band with a maximum at 1080 cm^{-1} which arises from $\text{Si}-\text{O}-\text{Si}$ bonds [7] formed through a combination of plasma and thermal oxidation processes taking place during polymerization. The asymmetry of this band indicates overlapping with other absorptions present in this region, a useful comparison being the spectrum of the film deposited from pure monomer vapor where a similar broad band is observed. A marked shift of the absorption band toward lower wavenumbers noted for Curve C (admixture of ammonia) again may be explained by an increase in $\text{Si}-\text{N}$ bond concentrations in the polymer due to the high reactivity of this gas mixture under plasma conditions.

A final, general comment on the infrared analyses is warranted. They show categorically that the composition of plasma polymer films

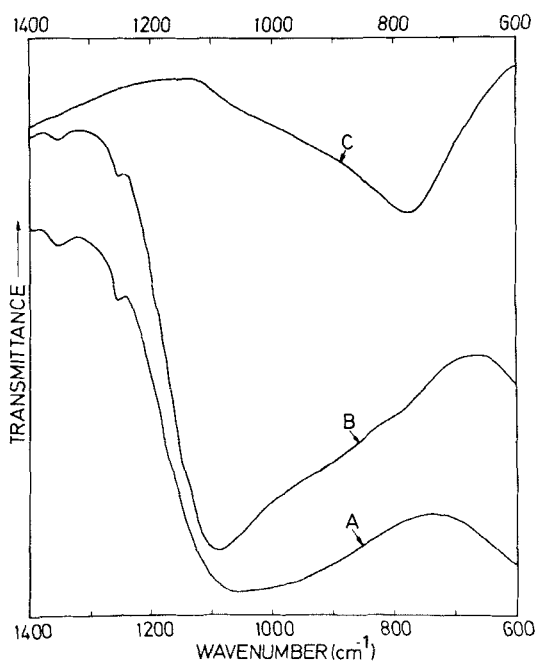


FIG. 7. Infrared ATR spectra of polymer films deposited from the mixture of various gases with HMCTSN vapor at the substrate temperature of 800°C: (A) monomer vapor, (B) with oxygen, and (C) with ammonia.

depends strongly on substrate temperature. The latter variable therefore is confirmed as a powerful tool for the modification and control of plasma polymer structure and physical properties. In particular, the balance of organic/inorganic content in such polymers can be shifted toward the inorganic by increasing T_s ; this is stated as a general observation, though we caution that at present the evidence rests solely on the organosilicone monomers involved in these studies. Broader studies, with wider ranges of monomers and substrates, are called for. The IR spectra also document the great complexity of reactions and interactions occurring during plasma polymerizations [4] and their equally complex dependence on substrate temperature. Their usefulness notwithstanding, IR data appear to have limited discrimination, particularly in the low wavenumber region, so that additional analytical techniques will be needed for a complete resolution of processes taking place.

CONCLUSIONS

The present investigation of plasma polymerization of organo-silicones has shown the following:

1. Deposition kinetics depend markedly on substrate temperature, T_s , and type of monomer, other parameters being kept constant.
2. The density of these plasma polymers, already high compared with conventional organosilicone polymers when $T_s \simeq 25^\circ\text{C}$, further increases with increasing substrate temperature.
3. Infrared spectra have shown that the chemical structure of these plasma polymers also depends strongly on T_s ; an increase in T_s eliminates hydrogen- and carbon-containing silyl groups, producing highly cross-linked materials of low organic content and high density.
4. The inherent properties of plasma polymerized organosilicones, and the ability to control these by substrate temperature and other independent variables of the reaction, indicate a high use potential for these materials; for example, as passivating, high temperature tolerant coatings for metals.

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REFERENCES

- [1] A. M. Wrobel and M. Kryszewski, J. Macromol. Sci.-Chem., **A12**, 1041 (1978).
- [2] A. M. Wrobel and M. Kryszewski, Polym. Prepr., **19**(2), 521 (1978).
- [3] H. P. Schreiber, Y. Tewari, and M. R. Wertheimer, Ind. Eng. Chem., Prod. Res. Dev., **17**, 27 (1978).
- [4] A. M. Wrobel, M. R. Wertheimer, J. Dib, and H. P. Schreiber, Polym. Prepr., **20**(1), 723 (1979); J. Macromol. Sci.-Chem., **A14**, 321 (1980).
- [5] R. G. Bosisio, M. R. Wertheimer, and C. F. Weissfloch, J. Microwave Power, **7**, 325 (1972).
- [6] R. G. Bosisio, M. R. Wertheimer, and C. F. Weissfloch, J. Phys., **E6**, 628 (1973).
- [7] D. R. Anderson, "Infrared, Raman and Ultraviolet Spectroscopy," in Analysis of Silicones (A. L. Smith, ed.), Wiley-Interscience, New York, 1974.

- [8] A. M. Wrobel, M. Kryszewski, and M. Gazicki, Polymer, 17, 678 (1976).
- [9] M. Gazicki, A. M. Wrobel, and M. Kryszewski, J. Appl. Polym. Sci., 21, 2013 (1977).
- [10] G. Turban and Y. Catherine, Thin Solid Films, 35, 179 (1976).
- [11] W. A. Pliskin, J. Vac. Sci. Technol., 14, 1064 (1977).
- [12] W. Kern and S. Rosler, Ibid., 14, 1082 (1977).

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