Mass Spectral Investigation of the Radio-Frequency Plasma Deposition of Hexamethyldisiloxane

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Experiments have been performed with the aim of enhancing our understanding of the reactions that take place within inductively coupled, radio-frequency (RF) plasmas of hexamethyldisiloxane (HMDSO). These plasmas have been investigated using a combination of mass spectrometry (MS) and deposition rate measurements. Thin films of HMDSO were deposited onto silicon substrates and analyzed by X-ray photoelectron spectroscopy (XPS). At low plasma power, the positive-ion MS data reveal that extensive molecular oligomerization takes place within the plasma gas phase. However, no significant formation of neutral oligomeric species was detected. XPS analysis revealed the surface stoichiometry of the deposit to be closer to that of the oligomers detected by MS than that of the starting compound (M). At higher plasma power, increased fragmentation of the monomer was observed, with a concomitant loss of the higher mass positively charged species. Again, no significant formation of neutral species of mass greater than M was detected. The deposition rate increased from *ca.* 6.5 to 15 ng s^{-1} over the power range investigated. We conclude that at low plasma power ion-molecule reactions are responsible for deposit formation. We propose that at high power the ionic component of these plasmas is still important, in terms of deposition.

1. Introduction

Thin, "pinhole-free" polymer-like films (termed plasma deposits) can be prepared from the non-equilibrium plasmas of volatile organic compounds.[1,2] These plasmas can be sustained by DC, AC, radio-frequency (RF) or microwave power. The plasma deposition process is attractive as an exact control over film thickness can be exercised (1−100 nm), film deposition can be conformal (even on substrates of complicated geometry), and polymerization takes place in an enclosed 'clean' environment without the use of solvents. A wide range of surface chemistries can be obtained through the selection of the starting compound(s) (the "monomer"), addition of an inert or reactive gas, and variation of the external plasma parameters. The potential applications of these materials are numerous[1,2] and still expanding,[3] with plasma deposition set to replace many conventional coating technologies.

The chemical structure of these materials has been the subject of numerous investigations. While the determination of their chemistry, and the influence that the plasma variables have on this chemistry is fairly straightforward, mechanistic understanding of how plasma deposits form is far from complete.[1,2,4] Plasma deposits of organosilicon compounds can be used as coatings for scratch and corrosion protection, as well as in gas diffusion membranes/barriers.[3,4] Hexamethyldisiloxane[4] (HMDSO) is an easy and safe monomer to handle (particularly so when compared with silane compounds) and has, hence, received considerable attention. In contrast to the extensive literature on the chemistry of HMDSO plasma deposits,[4−6] relatively little has appeared on the plasma-phase reactions of this monomer. Observations of how the plasma power (*P*), monomer flow rate (ϕ), sample bias, and temperature influence deposition rate and chemistry have allowed speculation on the types of reactions that give rise to product formation. The mechanisms proposed fall (broadly) into two distinct groups: those based on free-radical chemistry and those based on ion

chemistry.[6] Also, the site of deposit formation, in the plasma phase or at the substrate surface, has been the subject of some debate.[6]

This controversy still persists because no direct evidence (obtained from the plasma phase) has been available to support, or disprove, these proposed mechanisms. A very recent report[7] describes the use of gas chromatography−mass spectrometry (GC−MS) to analyze the condensable products collected from plasmas of HMDSO. While this type of study provides valuable information on the materials formed as a result of monomeric fragmentation and recombinations (of these fragments) in the plasma, it does not provide any further insight into the species in the plasma, nor how these react. This type of data can only be obtained from direct plasma-phase measurements. These measurements can be made by means of mass spectrometry (MS), which can be used to detect (directly) species implicated in polymer deposition.[8,9] MS has been used previously to investigate plasmas of silicon-containing organic molecules (silanes and siloxanes). Hays has described the use of MS to study RF plasmas of HMDSO[10] and methyltrimethoxysilane (MTMOS).[11] However, in neither of these reports were charged species, emanating from within the plasmas, differentiated from species ionized, by electron impact, within the spectrometer. This means that we cannot determine whether the species detected were formed by ion−molecule reactions or by recombination of neutral radical species. Furthermore, only fragments of the starting monomers were detected.

MS[12] and MS and light scattering[13] have been used to probe RF-sustained plasmas of silane (SiH$_4$). Silane plasmas are particularly suited for large area deposition of amorphous silicon (a: Si−H). Particulate formation within these plasmas is well-documented and limits manufacturing productivity and device reliability. In ref 12, neutral species, corresponding to 3Si, and positively charged species, containing up to 6Si, were detected by MS in a continuous plasma. No negatively charged species could be detected, because they are held within the discharge volume (by the sheath potentials which arise to prevent the

MS of RF Plasma Deposition of Hexamethyldisiloxane

J. Phys. Chem. B, Vol. 101, No. 18, 1997 **3615**
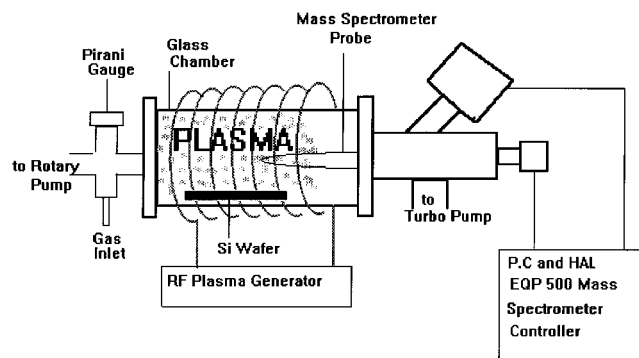
Figure 1. Schematic of plasma apparatus and mass spectrometer.

Figure 2. Electron impact mass spectrum of monomer.

Figure 3. Mass spectrum of the neutral portion of the plasma (obtained using electron impact). (A) $P/\phi = 1.9$ W min cm^{-3}; (B) $P/\phi = 7.3$ W min cm^{-3}.

escape of highly mobile electrons). In a power-modulated silane plasma, negative polysilicon hydride ionic clusters were observed up to 500 amu, the upper working limit of the mass spectrometer employed. In ref 13, a combination of MS and light scattering was used to show these negative ions to be the precursors to the particles that form within these plasmas.

In this paper we report a full MS characterization of the RF-sustained plasmas of HMDSO. We present clear evidence of cationic oligomerization within the gas phase and discuss this in the context of reaction mechanisms proposed previously. A scheme describing the major plasma-phase reactions of HMDSO is given. XPS is used to analyze the HMDSO plasma product, and we speculate on the relation between plasma-phase chemistry and deposit stoichiometry.

2. Experimental Section

The apparatus consisting of a plasma reactor interfaced to a mass spectrometer is illustrated in Figure 1. These were evacuated using a rotary pump and a turbomolecular pump, respectively. Species were allowed to diffuse from the plasma into the spectrometer through an aperture of 100 μm diameter. This arrangement enabled a base pressure of better than 10^{-3} mbar to be achieved in the reactor vessel and 10^{-8} mbar in the spectrometer. The sample vapor (HMDSO, purchased from the Aldrich Chemical Co.) was pumped through a needle valve to give a flow rate of 2.0 cm^3 min^{-1} (STP) and an operating pressure of 8×10^{-2} mbar. The plasma was sustained by a radio-frequency (13.56 MHz) signal generator and amplifier inductively coupled to the plasma chamber, the electrical power being in the range 5–20 W. The spectrometer was fitted with an ionization chamber so that it could be used to sample both neutral (by electron impact) and charged species emanating from the plasma, as well as for conventional residual-gas analysis in the absence of a plasma; in electron-impact experiments, the electron kinetic energy was 20 eV. The mass spectrometer was a quadrupole HAL EQP 500 model supplied by Hiden Analytical, which offers a range of *m/z* 0–500.

For deposition rate measurements, a probe containing a quartz crystal (exposed surface area 0.535 cm^2) was inserted into the plasma region, using a rigid support to ensure consistent positioning of the crystal. The signal from the probe was routed through to a deposition monitor. The deposition monitor, oscillator, and probe constituted the XTM/2 system by Leybold.

Because only small amounts of material could be prepared on a practical time scale, and because of strong adherence of the deposits (at the higher plasma powers used) to the substrate, XPS was chosen as the technique for analysis of the deposits. To prepare samples for XPS analysis, the quartz crystal was replaced with a methanol- and hexane-cleaned silicon wafer. The quartz mass balance was used to determine when 20 nm of material was deposited. This deposition time was then used
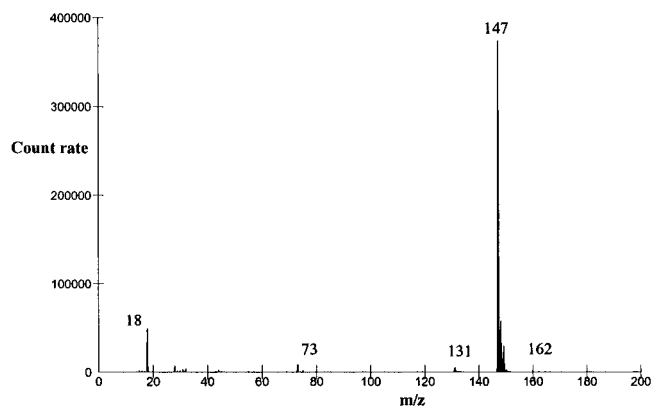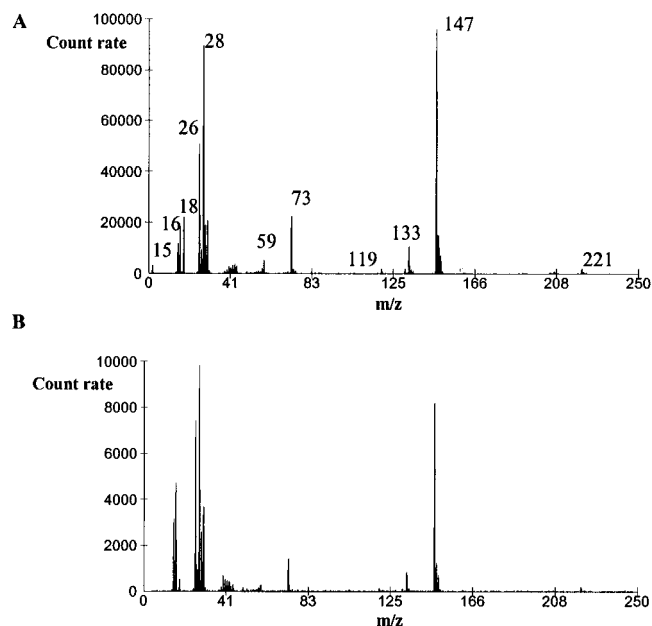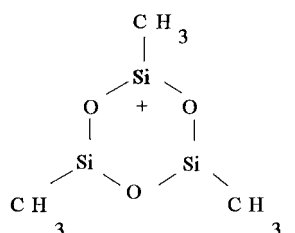
to deposit onto the silicon wafers and proved sufficient to yield films of thickness greater than the XPS sampling depth at a take-off angle of 30° relative to the sample surface. Samples were analyzed immediately after preparation. Samples were exposed to laboratory air for no more than 5 min after removal from the plasma reactor and before insertion into the XPS. XP spectra were acquired on a VG CLAM 2, using Mg Kα X-rays to excite a spectrum. The X-ray source was operated at 100 watts.

3. Results

3.1 Mass Spectrometry. *3.1.1. Electron Impact.* The electron impact mass spectrum of HMDSO was taken with the plasma switched off. This is presented in Figure 2. The principal signal within this spectrum arises from the monomer, minus a methyl group, and is seen at *m/z* 147. Also seen with considerable intensity is residual water at *m/z* 18. This is indicative of the slow desorption of water from the walls of the reactor vessel. Ions indicative of fragmentation of the HMDSO molecule are seen at *m/z* 73 and 131, but with far lower intensities. The low intensity of fragments, other than those closely related to the HMDSO molecule, indicates that under the conditions employed minimum fragmentation occurs. The instability of the molecular ion (M$^{\bullet+}$) is apparent from the low intensity of the peak seen at *m/z* 162 (<5% of the *m/z* 147

CHART 1: Structures Proposed for Neutral Species Detected in the HMDSO Plasma

| Mass / amu	Assignment
2	$H_2^{\cdot+}$
15	CH_3^+
16	$CH_4^{\cdot+}$
18	$H_2O^{\cdot+}$
26	$CH \equiv CH^{\cdot+}$
28	$CH_2 = CH_2^{\cdot+}$ and/or $Si^{\cdot+}$
30	$CH_3 - CH_3^{\cdot+}$
59	$(CH_3)_2 \overset{+}{S}iH$
73	$(CH_3)_3Si^+$
133	$HO - Si(CH_3)_2 - O - \overset{+}{S}i = CH_2$ and/or $H - Si(CH_3)_2 - O - \overset{+}{S}i(CH_3)_2$
147	$(CH_3)_3Si - O - \overset{+}{S}i(CH_3)_2$
221	$(CH_3)_3Si - O - Si(CH_3)_2 - O - \overset{+}{S}i(CH_3)_2$
207	$(CH_3)_3Si - O - Si(CH_3)_2 - O - \underset{H}{\overset{+}{S}}i(CH_3)$ and/or

signal). This instability has been noted elsewhere[14] and is an important feature in the subsequent interpretation of plasma-phase mass spectra.

3.1.2. Neutral Plasma-Phase Species. Electron impact was used to obtain mass spectra of the neutral species within plasmas of high and low plasma power density. These spectra are presented in Figure 3. In these, only a low intensity peak at m/z 221 was observed above the mass of the monomer (162). No signals were detected when the ionization source was turned off, confirming that there is no contribution from cations (diffusing from the plasma) to these spectra. In Chart 1 the most likely molecular formulae and possible structural assignments are provided for the more intense signals detected.

Comparison of these spectra with the electron impact mass spectrum (Figure 2) reveals that more extensive fragmentation of HMDSO has occurred within the plasma phase. The

observation of a signal at m/z 147 is taken to indicate the presence of intact monomer within these plasmas. By the same token, the signals seen at m/z 73 and 133 may indicate the presence of higher mass compounds that readily eliminate a methyl radical on ionization. From comparison of the two spectra in Figure 3, it is apparent that at higher plasma power (density) there is increased fragmentation of the monomer. This can be seen in the relative increases in the signal intensities at m/z 28, 26, 25, and 16 (*cf.* the ion at m/z 147).

3.1.3. Ionic Plasma Species. Mass spectra of the positive ions within high- and low-power plasmas are presented in Figure 4. It is immediately apparent that the variety of species detected is far greater than that seen in the neutral mass spectra. There are also a number of intense signals with masses greater than that of M. The highest of these is seen at m/z 383. Possible structural assignments for some of these species are given in Scheme 2 (discussion of this scheme is given later). Others (*e.g.* m/z 2−73, 133, and 207) correspond to structures given in Chart 1. The remaining ions can be readily assigned to structures of the following general types:

$$(CH_3)_3(OSi(CH_3)_2)_xCH_2^+$$

$$(CH_3)_3Si(OSi(CH_3)_2)_xOSi^+ = CH_2$$

$$(CH_3)_3Si(OSi(CH_3)_2)_xSi(CH_3)_2^+$$
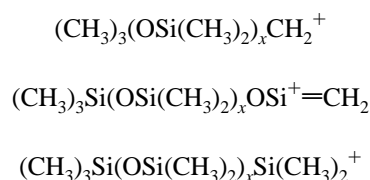
Increasing the plasma power density increases the proportion of lower mass fragments, as can be seen from the relative increase of the m/z 15, 16, 26, and 28 signals (*cf.* m/z 147). Peaks above m/z 330 have lost intensity and can no longer be clearly differentiated from the background noise.
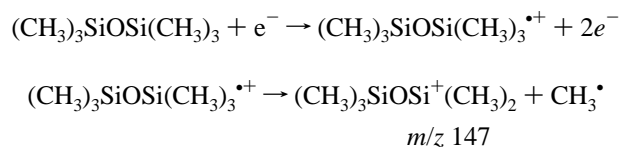
No negatively charged species were detected in these plasmas. The capability of the spectrometer to detect negative ions was confirmed in the analyses of Freon plasmas. We, therefore, conclude that either the stability of any anionic plasma species within the spectrometer is low or that none exist.

3.2. XPS. XPS was used to determine the surface stoichiometry of the high- and low-power plasma deposited films of HMDSO. The results are given in Table 1. From this table it can be seen that these deposits are low in carbon, relative to the monomer (C, 66%; Si, 22%; O, 11%).

3.3. Deposition Rate Measurements. The deposition rate was found to be constant with time at any specific P/ϕ. An increase in the deposition rate with increasing P/ϕ was observed as shown in Figure 5.

4. Discussion

The formation of an ion at m/z 147 in the electron-impact mass spectrum of HMDSO is readily explained by Scheme 1.

SCHEME 1

$$(CH_3)_3SiOSi(CH_3)_3 + e^- \rightarrow (CH_3)_3SiOSi(CH_3)_3^{\cdot+} + 2e^-$$

$$(CH_3)_3SiOSi(CH_3)_3^{\cdot+} \rightarrow (CH_3)_3SiOSi^+(CH_3)_2 + CH_3^{\cdot}$$
$$m/z\ 147$$

Electron-induced scission would also produce the same result, for electrons of lower energy, and might be considered more probable. Scheme 1 explains the low intensity of the m/z 162 ion in the spectrum of HMDSO (Figure 2). It is also very useful in helping to explain the types of reactions that occur in the plasmas of HMDSO.
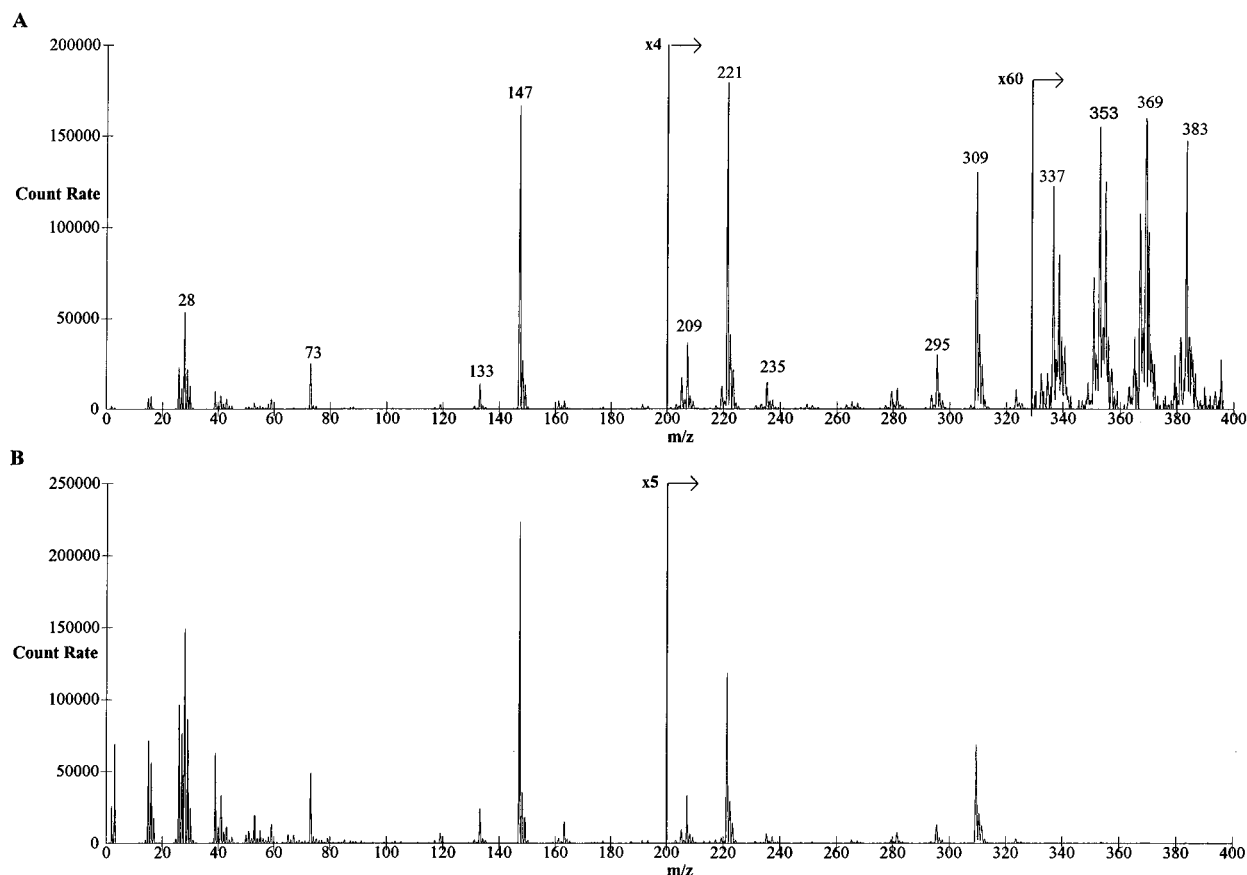
MS of RF Plasma Deposition of Hexamethyldisiloxane

J. Phys. Chem. B, Vol. 101, No. 18, 1997 **3617**

Figure 4. Mass spectrum of cations in the HMDSO plasma. (A) $P/\phi = 1.9$ W min cm^{-3}; (B) $P/\phi = 7.3$ W min cm^{-3}.
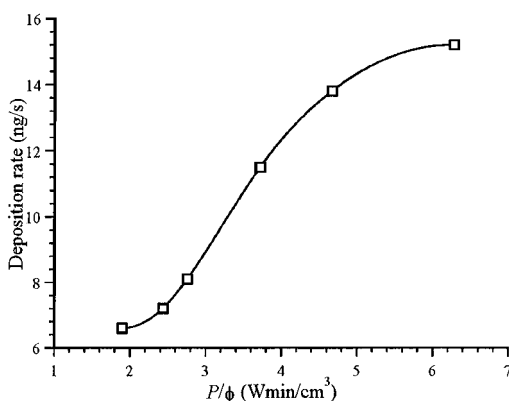

Figure 5. Rate deposition as a function of P/ϕ (W min cm^{-3}).

TABLE 1: XPS Elemental Analysis of HMDSO Deposits at Extremes of Power Density

P/ϕ	elemental composition in atomic percent		
	C	O	Si
1.9	57.3	17.0	25.6
7.3	57.0	18.1	24.9

4.1. Gas-Phase Oligomerization. It is most appropriate to consider the low-power plasma of HMDSO first. The constant electron flux in the plasma will ensure ionization (and fragmentation) of the monomer. We propose that the ionized monomer eliminates a methyl radical, giving rise to the m/z 147 ion. This is shown as step A in Scheme 2. Decomposition of the m/z 162 ion to yield a radical of 147 amu and a methyl cation (m/z 15) is not thought to be a major fragmentation pathway. (In Figure 4A only a weak signal is seen at m/z 15.) The m/z 147 cation can subsequently react with an "intact"

HMDSO molecule, M (step B), giving rise to an ion of m/z 309, which is seen with considerable intensity in Figure 4A. This species could rearrange, eliminating tetramethylsilane (neutral), as shown in step C. The resultant charged fragment will be seen at m/z 221 in the positive ion mass spectrum. This species could, in turn, further react with another HMDSO molecule, giving rise to a positively charged species of m/z 383 (step D). This part of our scheme is very similar to that proposed by Wróbel,[14] on the basis of GC−MS data from the extractable portion of an HMDSO deposit. It differs in step C, in that Wróbel proposed elimination of a trimethylsilyl cation. This would produce a neutral species of m/z 221. This process is shown in Scheme 2 as step E. However, the low intensity of the neutral species at m/z 221 (Figure 3A) indicates that this is a minor reaction pathway.

4.2. Fragmentation. Other high-mass species seen in Figure 4A can be explained by loss of CH$_2$ from larger ions. This is shown in step F for the m/z 383 ion, which yields the m/z 369 ion. The m/z 147 ion may also fragment to produce species seen at lower mass in Figures 3A and 4A. Homolytic cleavage of the Si−O bond produces a trimethylsilyl radical of m/z 73, seen in Figure 3A (step G in Scheme 2), and heterolytic cleavage produces a trimethylsilyl cation, seen in Figure 4A (step H in Scheme 2). Further fragmentation accounts for the smaller cationic/neutral species detected (Figures 3A and 4A).

The extent of fragmentation of the m/z 147 (versus "molecular oligomerization") is determined by the power density of the plasma. High-power density results in increased fragmentation and this manifests in a relative loss of intensity in the higher mass species (Figure 4B) and a relative increase in the intensities of lower mass species (Figures 3B and 4B).

4.3. Gas-Phase Chemistry−Solid-Phase Product. The increase in deposition rate seen as the plasma power increases

SCHEME 2
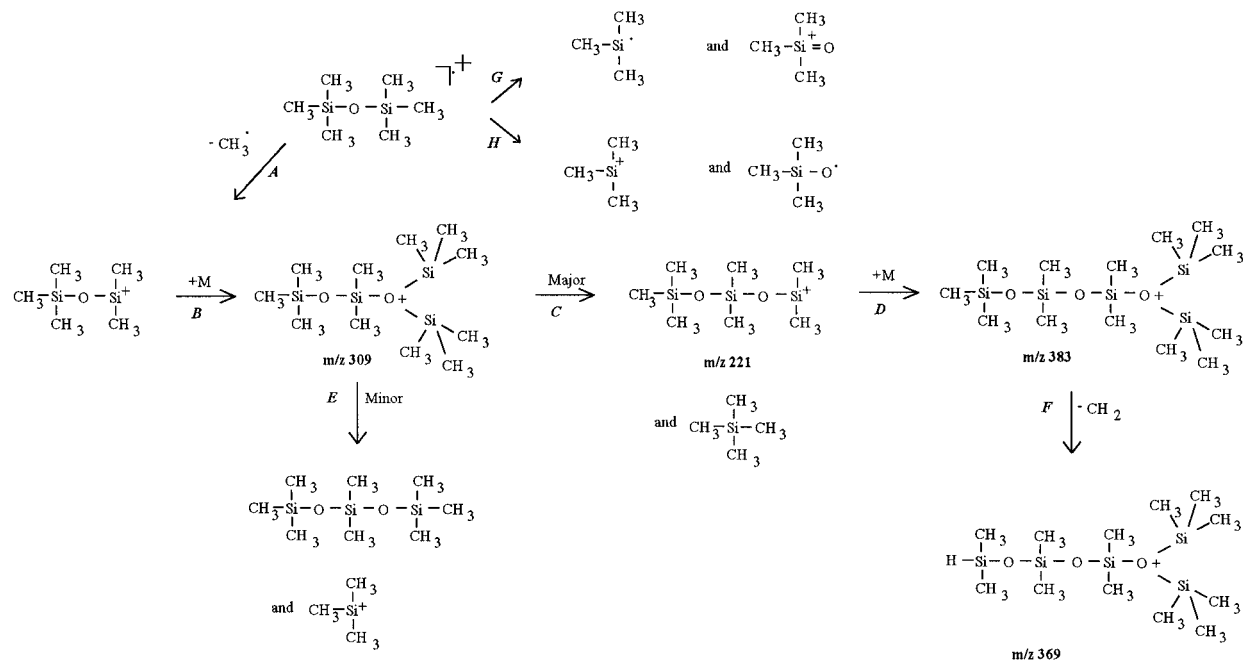
is consistent with previous observations.[4,8,9] In the plasma polymerization of unsaturated alkyl methacrylates[8] and propenoic acid,[9] the rate of "polymer" deposition increased with plasma power. In these systems, a strong correlation has been drawn between plasma-phase chemistry and the chemistry of the deposits. At low plasma power, positively charged species representing dimers[8] and dimers and trimers[9] of the starting compounds were detected by plasma mass spectrometry. In the plasma product very high levels of functional group retention, *ca.* 60−70% of ester[8] and acid,[9] were measured by XPS. As the plasma power increased, the abundance of these dimeric/trimeric species dramatically decreased, and the level of functional group retention also significantly dropped. At higher plasma power, new functionalities were introduced into the deposit, namely C−OH, C−O−C, C=O, and O−C−O, representing greater fragmentation of the starting compounds and also, possibly, modification of the deposited material, under the influence of greater ion bombardment and VUV−UV exposure.

The low-power plasma deposits of alkyl methacrylates and propenoic acid described in refs 8 and 9 are oily materials, and even in deposits obtained at higher power there is no discernible morphology by SEM/AFM. This clearly distinguishes these deposits, and the conditions under which they are obtained, from the deposits obtained from SiH_4 described in refs 12 and 13. In the present study, HMDSO plasma deposits were obtained using the same apparatus and low power conditions employed in refs 8 and 9. While negative ion chemistry is strongly implicated in the formation of solid-phase particulates, under the conditions used in this study, we believe the role of positively charged species to be more important in film deposition. Once we allow for the transmission function of the EQP mass spectrometer, between $1/m$ and $1/m^2$,[15] it is clear that the oligomerization seen in the positive ions is a major reaction pathway. These oligomeric species, by virtue of their mass, are likely to condense at available surfaces. They are also charged, and so may be attracted to the surfaces in contact with the plasma. (All surfaces in contact with the plasma will acquire a negative potential.[2]) Further, the stoichiometry of the deposit, as determined by XPS, is closer to that of the oligomeric species (e.g. m/z 221) than that of the starting compound.

At high plasma power, although there is still some oligomerization taking place within the plasma, this is obviously less important. Increased power produces more fragmentation of the monomer. This result has been reported previously in plasmas of alkyl methacrylates[8] and carboxylic acids.[9] The increased deposition rate shown in Figure 5 must, therefore, arise from an increased flux of smaller fragments arriving at the substrate surface. Whether these are charged (*i.e.* cations) or neutral species cannot be determined unambiguously from the data available. However, the following points are worth considering.

(1) The low carbon content of the deposit suggests that preferential loss of $CH_3^\bullet$ is still taking place. According to Scheme 2 the elimination of such a species from an already charged species (*e.g.* see step A) results in the formation of a cation. The mass spectrum in Figure 4A reveals that there is an abundance of low mass ions, and these could account for deposit formation.

(2) In the plasma treatment of polymers by inert and simple reactive gases, it is well-established that it is the ionic (and UV) components of the plasma that are primarily responsible for modification.[16] Positively charged species experience a considerable net attraction to surfaces in contact with plasma. This arises from the difference between the plasma potential, V_p, usually several volts positive, and the substrate potential, V_s, which can be as much as a few tens to a few hundreds of volts negative.

(3) No (abundant) species larger than the monomer are seen in the neutral mass spectrum, and hence, we can rule out (significant) polymer formation in the plasma phase by free-radical chemistry.

The argument has been put forward (elsewhere)[17] that charged species arriving, from the plasma, at a substrate surface create free-radical sites and that it is these that are primarily responsible for deposit growth. In this instance, this seems unlikely, given that there is no site of unsaturation within the 'intact' HMDSO compound. Such a site is required for chain growth to be propagated from the substrate surface. However, in this type of system, the role that radicals play still cannot be ignored: the presence of free radical centers in these materials has been well-demonstrated.[2] These centers probably lead to the incor-

MS of RF Plasma Deposition of Hexamethyldisiloxane

J. Phys. Chem. B, Vol. 101, No. 18, 1997 **3619**

poration of some atmospheric oxygen and condensed HMDSO, as well as the formation of high densities of cross-links within the material.

5. Conclusions

Evidence is presented for the importance of ions in the formation of deposits from RF plasmas of HMDSO.

At low plasma power, extensive oligomersiation is observed in HMDSO- plasmas, and the stoichiometry of these oligomeric species correlate well with the surface stoichiometry of the deposit. A mechanistic scheme is presented which describes the major plasma-phase reactions.

Increased plasma power results in less plasma-phase oligo-merization and greater fragmentation of HMDSO. The deposition rate is observed to increase. However, no significant neutral free-radical chemistry is observed in the plasma phase, and we argue that the arrival of ions at the substrate surface represents a significant contribution to deposit formation. The increased flux (number) of these ions arriving at the surface will directly contribute to the higher deposition rates. Ion bombardment will result in the formation of radical centers, which can react with gas phase species, also increasing the deposition rate.

References and Notes

(1) Morosoff, N. In *Plasma Deposition, Treatment and Etching of Polymers*; d'Agostino, R., Ed; Academic Press: London 1991; Chapter 1.

(2) Yasuda, H. K. *Plasma Polymerisation,* Academic Press: New York, 1985.

(3) Taylor, C. E.; Boerio, F. J.; Clarson, S. J.; Zeik, D. B. *Advanced Coatings Technology,* ESD, The Engineering Society: Ann Arbor, MI, 1993; p 219.

(4) Wróbel, A. M.; Wertheimer, M. R. In *Plasma Deposition, Treatment and Etching of Polymers*; d'Agostino, R., Ed; Academic Press: London 1991; Chapter 3.

(5) Alexander, M. R.; Short, R. D.; Jones, F. R.; Stollenwerk, M.; Zabold, J.; Michaeli, W. *J. Mater Sci.* **1996**, *31*, 1867.

(6) Vasile, M. J.; Smolinski, G, *J. Electrochem. Soc., Electrochem. Sci. Technol.* **1972**, *119*, 4, 451.

(7) Sarmadi, A. M.; Ying, T. H.; Denes, F, *Eur. Polym. J.* **1995**, *31*, 9847.

(8) Ameen, A. P.; O'Toole, L.; Short, R. D.; Jones, F. R, *J. Chem. Soc., Faraday Trans.* **1995**, 1363.

(9) O'Toole, L.; Beck, A. J.; Ameen, A. P.; Jones F. R.; Short, R. D, *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3907.

(10) Hays, A. K, *Proc. Electrochem. Soc.* **1982**, *82−86*, 75.

(11) Hays, A. K., *Thin Solid Films* **1981**, *84*, 401.

(12) Howling, A. A.; Sansonnens, L.; Dorier, J-L.; Hollenstein, Ch., *J. Appl. Phys.* **1994**, *75* [3(1)], 1340.

(13) Hollenstein, Ch.; Dorier, J-L.; Dutta, J.; Sansonnens, L.; Howling, A. A, *Plasma Sources Sci. Technol.* **1994**, *3*, 278.

(14) Wróbel, A. M.; Kryszewski, M.; Gazicki, M, *J. Macromol. Sci. Chem.* **1983**, *A.20*, 583.

(15) Hatton, P., Private Communication, Hiden Analytical Ltd, Warrington, WA5 5TN, UK.

(16) Liston, E. M.; Martinu, L.; Wertheimer M. R. In *Plasma Surface Modification of Polymers: Relevance to Adhesion;* Strobel, M., Lyons, C. S., Mittal, K. L., Eds.; VSP: Utrecht, Netherlands, 1994.

(17) Denaro, A. R.; Owens, P. A.; Cranshaw, A. In ref 6.