the weight loss still goes on; this may possibly be ascribed to the thermal decomposition of HCN itself. These results show that the elimination of excess carbon under ammonia is optimum at about 1000 °C. Reaction 19, like any solid–gas reaction, is highly sensitive to the surface area of the sample,[9] and the large excess carbon still present after the pyrolysis of PVSZ1 in ammonia is certainly related to the compactness of this sample; in addition, the larger amount of vinyl groups in PVSZ1 compared to PVSZ2 leads to the formation of a larger amount of excess carbon.

In the case of PMSZ, elemental analysis indicates the presence of 8.5 wt % carbon at 750 °C, whereas no HCN is detected. The ^{13}C solid-state NMR (Figure 7) shows that, after heating at 750 °C under ammonia, the remaining carbon atoms are still in the sp^3 hybridization state; in addition, the nitrogen content of the pyrolysate increases from 750 to 1350 °C. Thus the amination stage of the precursor is not complete at 750 °C (probably due to the high heating rate used), and ammonia continues to substitute the Si–C bonds above 750 °C.

Conclusion

The thermal reactions occurring during the pyrolysis of preceramic polysilazanes depend on the nature of the functional groups of the precursors.

In an inert atmosphere, mineralization involves mainly free-radical reactions; large amounts of excess carbon are observed when the precursors possess unsaturated carbon groups, probably due to their reactivity toward free radicals.

Under ammonia, different mechanisms may be distinguished depending on the nature of the groups borne by the silicon atoms.

In all cases, complete amination of silicon occurs between 300 and 750 °C, before the thermal decomposition of ammonia. The mechanism of this substitution is likely nucleophilic in the case of Si–H bonds, whereas homolytic cleavages of Si–C bonds certainly occur in the case of carbon substituents.

The possibility of hydrogen abstraction from ammonia favors the escape of hydrocarbons: thus, methyl and phenyl groups are quantitatively removed as methane and benzene, respectively, and amination and carbon removal coincide. On the other hand, vinyl groups are not completely displaced by ammonia and lead to the formation of unsaturated excess carbon; above 750 °C, this excess carbon reacts with ammonia decomposition products, leading to an escape of hydrogen cyanide.

Registry No. PMSZ, 105009-41-4; PSSZ, 144043-04-9; PVSZ, 144043-05-0; Ar, 7440-37-1; NH_3, 7664-41-7.

Plasma-Enhanced Chemical Vapor Deposition of Bulk Organosilicon Solids Using Hexamethyldisilane Precursor

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Plasma polymerization of hexamethyldisilane ($[CH_3]_3SiSi[CH_3]_3$) at low radio frequency powers results in the formation of a fine brown powder. On prolonged exposure to air, this deposit changes in appearance to bright yellow. Freshly collected organosilicon material and its subsequent ageing have been investigated by XPS, FTIR, XRD, and solid-state NMR. A high proportion of $(CH_3)_xSi$ (x = 1, 2,3) linkages and trapped reactive centers are identified in the gathered material; these species readily undergo oxidation and cross-linking on standing in the laboratory atmosphere.

Introduction

Molecules injected into a glow discharge may undergo activation and fragmentation while subjected to the influence of electrons, metastables, radicals, ions, and photons. Under optimum conditions, successive dissociation and recombination of the reactive components within a plasma can yield extended molecules in the gas phase, with concurrent attachment of fragments to an adjacent substrate.

Plasma-deposited organosilicon materials are reported to possess high dielectric strengths.[1] Tetramethylsilane ($Si[CH_3]_4$),[2,3] phenylsilane ($[C_6H_5]SiH_3$),[4] and trimethylvinylsilane ($[CH_3]_3Si[CHCH_2]$)[5,6] are among some of the carbosilane monomers previously used. Silylmethyl groups, $(CH_3)_xSi$ (x = 1, 2, 3) have been invoked to play a major role during the plasma polymerization of organosilanes.[7] However, none of the above-mentioned precursors are reported to readily yield vast amounts of solid product. In this study we have chosen hexamethyldisilane ($[CH_3]_3SiSi[CH_3]_3$) as the monomer. This molecule contains a weak Si–Si linkage which should make it much more susceptible toward plasma-enhanced chemical vapor deposition (PECVD) relative to monosilicon-based pre-

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cursors. The collected material and its subsequent ageing have been characterized by XRD, FTIR, XPS, and solid-state NMR.

Experimental Section

A small amount of hexamethyldisilane (98%, Aldrich Chemical Co.) was transferred under a nitrogen atmosphere into a monomer reservoir and then purified by multiple freeze-pump-thaw cycles. The glow discharge reactor used in this study is similar to that previously described.[8] It was fitted with a glass substrate, a monomer inlet, a vacuum pressure gauge, a two-stage rotary pump with a liquid nitrogen cold trap, and a matching network for inductive coupling to a 13.56-MHz radio frequency source. First the system was pumped to 2×10^{-2} Torr. The leak rate was calculated[9] to be less than $2.6\ 10^{-10}$ kg/s (the molecular composition of air being taken as 79% N_2 and 21% O_2). Hexamethyldisilane was introduced into the reaction vessel via a fine control needle valve at a pressure of 1×10^{-1} Torr. The monomer flow rate (F_m) was calculated to be 4.3×10^{-8} kg/s. These operating conditions ensured that the organosilane precursor accounts for at least 99.4% of the gaseous contents within the reaction chamber. A 5-W plasma (i.e., at a (W/F_m) ratio of 1.2×10^8 J/Kg) was ignited 5 min after the introduction of the monomer. On completion of deposition, the reactor was sustained under vacuum (2×10^{-2} Torr) for a further 5 min. Fresh, and samples left in contact with air were analyzed by microanalysis (Carlo Erba elemental analyzer Model 1106), XPS, FTIR, XRD, and solid-state NMR. Shorter ageing times were needed for XPS studies since it is a highly surface sensitive technique. Typically, XPS analysis showed no variation after 5 days, whereas FTIR and NMR spectra did not reach their limiting spectral features until at least a month following deposition.

FTIR spectra were recorded on a Mattson Polaris spectrometer. The collected powder was mixed with KBr and pressed into a disk. Typically, 100 scans were accumulated at a resolution of 4 cm^{-1}.

X-ray photoelectron spectra were acquired on a Kratos ES200 surface analysis instrument. Magnesium Kα radiation (1253.6 eV) was used as the excitation source with electron detection in the fixed retarding ratio (22:1) analyzer mode. The gold $4f_{7/2}$ level at 83.8 eV had a full width at half-maximum (fwhm) of 1.2 eV. XPS measurements were taken with an electron takeoff angle of 30° from the surface normal. No radiation damage to the samples was observed during the typical time scale involved in these experiments; this was checked by examining the peak profiles as a function of X-ray exposure. Data accumulation and component peak analysis were performed on a PC computer, using linear background subtraction and Gaussian fits with fixed full width half-maxima (fwhm). All binding energies are referenced to the hydrocarbon component at 285.0 eV[2]. For these experiments, the instrumentally determined sensitivity factors were such that for unit stoichiometry, the C(1s):O(1s):Si(2p) intensity ratio is 1:0.55:1.05.

Solid-state NMR spectra were obtained by using a Varian VXR-300 spectrometer and a Doty Scientific magic angle spinning (MAS) probe. Silicon-29 spectra were recorded at 59.6 MHz and carbon-13 at 75.4 MHz. An external sample of tetramethylsilane was used as the chemical shift reference in both cases. Cross-polarization (CP) spectra were obtained taken with a 3-ms contact time and a relaxation delay of 2 s. Silicon-29 spectra were additionally acquired following 90° pulses (of 4 μs) with relaxation delays of 5 and 60 s. In all cases sample spin rates were about 4 kHz.

Results

Freshly deposited powder was found to change from brown to yellow after prolonged exposure to air. This material was highly resistant toward chemical attack (e.g., alkaline solutions), and it was also found to be mechanically tough. Microanalysis gave a H/C ratio of 2.3. Powder X-ray diffraction measurements yielded no evidence for any degree of crystallinity in either the unaged or oxidized powders.

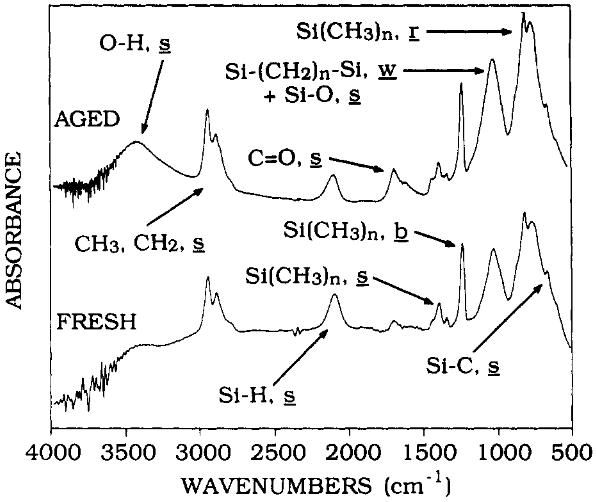

Figure 1. Infrared spectra of the plasma deposited powder before and after ageing: stretching (s), rocking (r), bending (b), and wagging (w).

FTIR. Hexamethyldisilane possesses the following infrared absorption bands:[10] 2951 (C-H asymmetrical stretching in CH_3), 2893 (C-H symmetrical stretching in CH_3), 1246 (CH_3 symmetric bending in $Si(CH_3)_n$), 835 (CH_3 rocking in $Si(CH_3)_n$), and 721, 690, and 607 cm^{-1} (Si-C stretching). The Si-Si stretch is infrared inactive.

Typical FTIR spectra of the plasma deposit generated from HMDS are shown in Figure 1 for both fresh and aged powder. CH_3 stretching bands are known[11] to occur at 2962 (C-H antisymmetrical stretching) and 2872 cm^{-1} (C-H symmetrical stretching). Whereas methylene groups (CH_2) in aliphatic and nonstrained cyclic hydrocarbons exhibit C-H antisymmetrical and symmetrical stretches at 2926 and 2853 cm^{-1}, respectively[11] (the exact positions may vary across a range of ±10 cm^{-1}). It should be noted that in strained rings, methylene stretching frequencies have been reported to increase. Therefore it can be concluded that the 2951- and 2895-cm^{-1} bands recorded in the FTIR spectra of the freshyl deposited material arise as a result of the overlap between CH_3 and CH_2 stretching frequencies.

Silicon-related absorption bands are widely described in the literature.[1-5,12] The following bands were assigned for the freshly collected material: 2104 (Si-H stretching), 1408 (Si-CH_3 antisymmetrical stretching and/or CH_2 scissoring in $Si(CH_2)_n$), 1356 (methylene twisting and wagging vibrations), 1254 (CH_3 symmetrical bending in $Si(CH_3)_n$), (1044 cm^{-1} to Si-O-Si and/or Si-O-C and/or CH_2 wagging in $Si-(CH_2)_n-Si$), 835 (CH_3 rocking in $Si(CH_3)_n$ (n = 2, 3)), 785 (CH_3 rocking in $Si(CH_3)_n$ (n = 1, 2)), and 685 cm^{-1} (Si-C stretching).

It is interesting to note that all the cited infrared absorptions for the fresh powder shift to higher frequencies on ageing; this is consistent with the assumption that reactive centres in the solid product undergo cross-linking. There is also strong evidence for bulk oxidation, since the following additional bands emerge: 3426 (OH stretching[1]), 1717 (C=O stretching[11]), 1632 (antisymmetrical stretching mode of C=O in carboxylates[11]), and the 1044 cm^{-1} band increases in intensity, which signifies the presence of Si-

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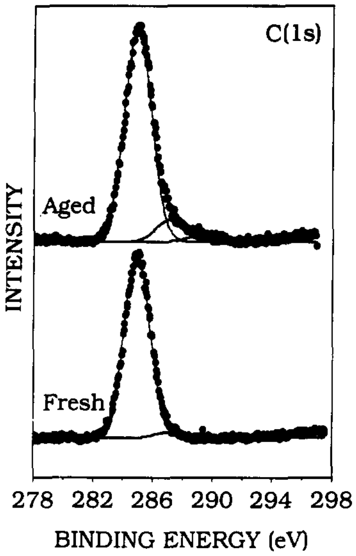

Figure 2. C(1s) XPS spectra before and after ageing.

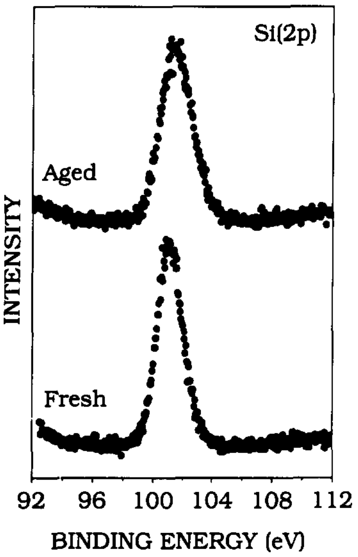

Figure 3. Si(2p) XPS spectra before and after ageing.

O–Si and/or Si–O–C bonding. Also it is highly likely that the 1632-cm^{-1} band may have an alkene component, since the C=C stretching mode of unconjugated olefins are known to possess a moderate to weak absorption[1] at 1667–1640 cm^{-1}, this would be consistent with trapped carbon centre free radicals undergoing recombination to form double bonds.

XPS. Figures 2–4 show XPS spectra of fresh powder deposited for 1 h at 5 W onto a glass slide and its subsequent ageing. In the C(1s) region, the main peak at a binding energy of 285.0 eV can be assigned to C–H, C–C, and C–Si environments.[13,14] There is also a very slight shoulder at 287.9 eV, which is probably due to a small amount of surface oxidation during transport through air to the electron spectrometer (a corresponding O(1s) signal at 533.2 eV is observed). A strong peak centred at 101.1 eV was found for the Si(2p) core level, this is characteristic of Si–H and Si–C bonds.[13,14] From the XPS data, the relative composition of the fresh material was estimated to be 75% carbon, 21% silicon, and 4% oxygen (XPS can not detect the amount of hydrogen).

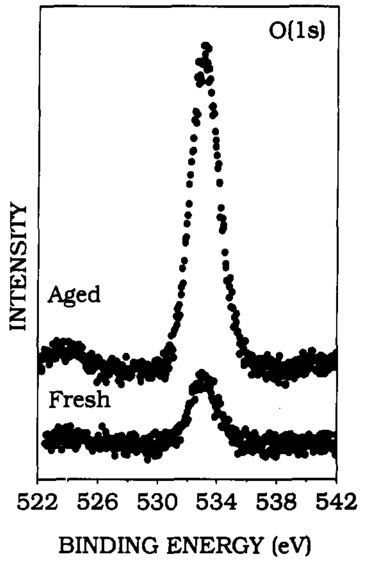

Figure 4. O(1s) XPS spectra before and after ageing.

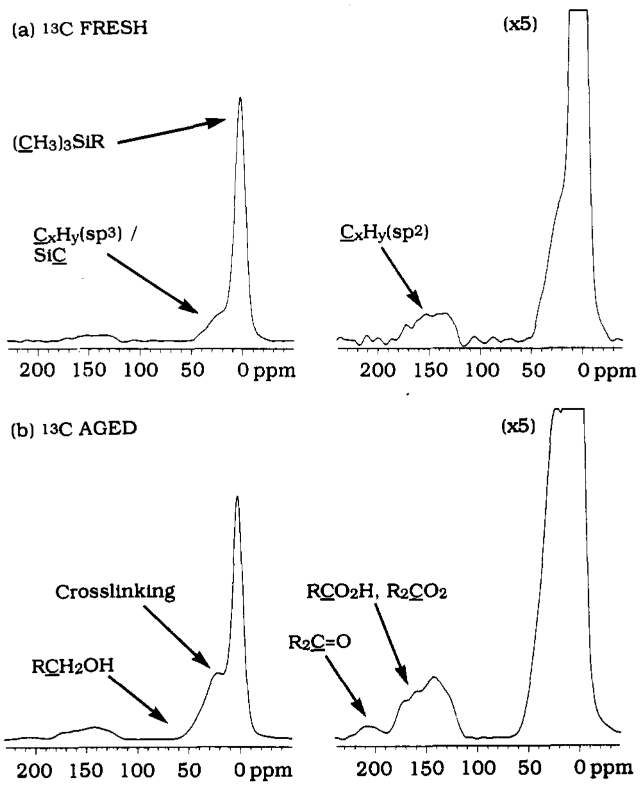

Figure 5. ^{13}C solid-state NMR spectra: (a) before and (b) after ageing (extra features indicated).

On ageing, the C(1s) envelope develops a pronounced shoulder toward greater binding energies. This can be attributed to the presence of carbon singly bonded to one oxygen atom (–*C*–O– ~286.6 eV), carbon singly bonded to two oxygen atoms or carbon doubly bonded to one oxygen atom (–O–*C*–O–, -*C*=O ~287.9 eV) and carboxylate groups (–O–*C*=O ~289.0 eV).[15] The Si(2p) peak center also increases in value to 101.4 eV with an accompanying shoulder at higher binding energy. Again this can be taken as evidence for silicon bonded to oxygen (*Si*–O at 102.2 eV and *Si*O_2 at 104.1 eV).[16] Following oxidation, the relative

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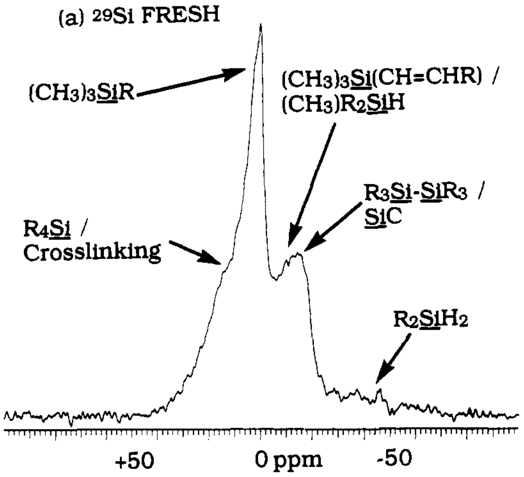
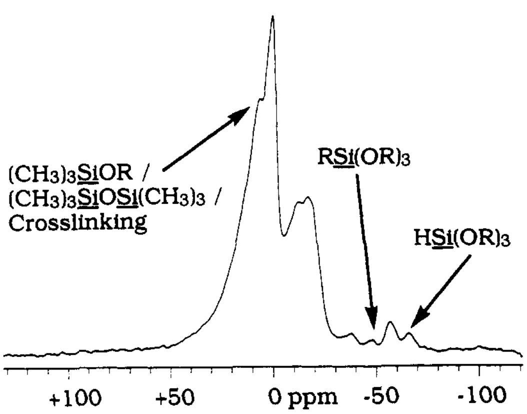


(a) ^{29}Si FRESH



(b) ^{29}Si AGED

Figure 6. ^{29}Si solid-state NMR spectra: (a) before and (b) after ageing (extra features indicated).

atomic composition was calculated to be 66% carbon, 18% silicon, and 15% oxygen.

Solid-State NMR. All the NMR measurements are referenced with respect to tetramethylsilane, $(CH_3)_4Si$. The numerous ^{13}C and ^{29}Si NMR chemical shifts referred to in this section, have been assigned by using literature data for model compounds.[17,18] ^{13}C and ^{29}Si spectra are shown in Figures 5 and 6, respectively. The band shapes are consistent with contributions from a wide variety of chemical species. In both the ^{13}C and ^{29}Si spectra, the most intense peak is around 0 ppm, arising from chemical environments similar to those found in tetramethylsilane. In other words, the major constituent of the deposited material is a silicon center which is bound to a number of methyl groups.

In the ^{13}C spectrum there is a high frequency shoulder between 20 and 50 ppm indicative of sp^3 carbon atoms within a hydrocarbon chain. Pure silicon carbide (depending on the polytype) also has characteristic peaks in this region.[19] The weak ^{13}C signal between 120 and 180 ppm suggests a small degree of unsaturation or oxygenation.

Following prolonged exposure of the material to air, there was a marked increase in intensity of ^{13}C environments between 190 and 210 ppm (ketones and aldehydes) and 150 and 185 ppm (carboxylic acids and esters). There is also a broadening of the main shoulder due to alcohols (60 to 70 ppm) and quaternary carbons (30 to 55 ppm).

The corresponding ^{29}Si NMR spectra for the freshly deposited plasma polymer consists of peaks at 6.6, 1.0, −9.2, −13.6, and −36.0 ppm. In general, organosilicon compounds of the type $R^1R^2R^3R^4Si$ yield ^{29}Si chemical shifts varying from −4.5 to +20.0 ppm. Extension of the alkyl chain results in a shift to high frequency, as illustrated by the following model compounds: $(CH_3)_4Si$ at 0.0 ppm, $(CH_3)_3Si(C_2H_5)$ at 1.6 ppm, $(CH_3)_2Si(C_2H_5)_2$ at 4.6 ppm, $(CH_3)Si(C_2H_5)_3$ at 6.5 ppm, and $(C_2H_5)_4Si$ at 7.1. Therefore likely candidates for the peak centered at 6.6 ppm are silicon centers bonded to hydrocarbon chains where not more than one R chain is a methyl group, as invoked by the following series of model compounds: $(C_2H_5)_3Si(CH_3)$ 6.5 ppm, $(C_2H_5)_3Si(C_2H_5)$ 7.1 ppm, $(C_2H_5)_3Si(n\text{-}C_4H_9)$ 6.9 ppm. The signal at +1.0 ppm can be attributed to $(CH_3)_3Si$ functionality located at hydrocarbon chain ends, as suggested by the following set of model compounds: $(CH_3)_4Si$ at 0.00 ppm, $(CH_3)_3Si(C_2H_5)$ at 1.6 ppm, $(CH_3)_3Si(n\text{-}C_3H_7)$ at 0.7 ppm, $(CH_3)_3Si(n\text{-}C_4H_9)$ at 0.6 ppm, $(CH_3)_3Si(n\text{-}C_5H_{11})$ at 0.2 ppm, and $(CH_3)_3Si(CH_2CH_2CH(CH_3)_2)$ at 0.9 ppm. The shoulder at −9.2 ppm could be either from silicon centers with unsaturated carbon centers attached to the β position from the $(CH_3)_3Si$ group of the type $(CH_3)_3Si(CH{=}CHR)$ where R = H or CH_3 or from $(CH_3)R_2SiH$ provided R has an alkyl chain containing at least two $(-CH_2-)$ linkages, as seen from the following list of model compounds: $(CH_3)(n\text{-}C_3H_7)_2SiH$ at −10.9 ppm, $(CH_3)(n\text{-}C_3H_7)_2SiH$ at −10.9 ppm, $(CH_3)(n\text{-}C_4H_9)_2SiH$ at −9.8 ppm, $(CH_3)(n\text{-}C_5H_{11})_2SiH$ at −9.8 ppm, $(CH_3)(n\text{-}C_6H_{13})_2SiH$ at −9.9 ppm. Hexamethyldisilane, $(CH_3)_3Si\text{-}Si(CH_3)_3$ gives a ^{29}Si NMR peak at −20.5 ppm, and therefore the feature at −13.6 ppm could have some contribution from Si–Si linkages. However, silicon carbide types species are also known to occur in this region.[19] The weak feature at −36.0 ppm could be some form of $R^1R^2SiH_2$ linkage, as given by the following model compound: $(CH_3)_2SiH_2$ at −37.7 ppm.

On ageing, there is a marked increase in intensity of the shoulder at 6.9 ppm in the ^{29}Si spectrum. In general, $(CH_3)_3SiOR$ species have characteristic chemical shifts in this vicinity, e.g., $(CH_3)_3SiO(C_2H_5)$ at 7.4 ppm. Other possibilities include $(CH_3)_3SiOSi(CH_3)_3$ at 6.0 ppm. The following series of compounds can be regarded as models for the varying degrees of cross-linking around a Si atom: $(CH_3)_3SiR^1$ at ~1 ppm, $(CH_3)_2SiR^1R^2$ at ~4 to 5 ppm, $(CH_3)SiR^1R^2R^3$ at ~6 to 7 ppm, and $SiR^1R^2R^3R^4$ at ~7 to 8 ppm; therefore any significant degree of cross-linking would also result in a contribution toward the shoulder at 6.9 ppm. Small components to the low-frequency side of −40 ppm are assigned to silicon bound to increasing numbers (2, 3, or 4) of oxygen atoms, as seen from the following model compounds: $(n\text{-}C_4H_9)Si(OC_2H_5)_3$ at −47.4 ppm, $n\text{-}C_3H_7Si(OC_2H_5)_3$ at −47.0 ppm, $C_2H_5Si(OC_2H_5)_3$ at −45.9 ppm, $(CH_3)Si(OC_2H_5)_3$ at −45.5 ppm, $(CH_3)Si(OCH_3)_3$ at −41.5 ppm, and $HSi(OC_2H_5)_3$ at −66.0 ppm. The −56.6 ppm peak could be attributed to some form of cross-linking, e.g., $(CH_3)_2Si[CH(n\text{-}C_3H_7)]_2$ at −59.8 ppm.

Discussion

In most cases, plasma-enhanced chemical vapor deposition yields fairly low amounts of product; however, with hexamethyldisilane it was surprisingly easy to obtain substantial quantities of solid material. This can be attributed to the high reactivity of this particular organosilicon monomer, which arises from the chromophoric character of the Si–Si bond. Electron–molecule and photon–molecule reactions are widely recognized as being

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two of the key processes responsible for ionization and dissociation within a glow discharge. Free radicals can be generated from thermal,[20] ultraviolet-initiated,[21] and electron-induced decomposition[22] of HMDS:

$$(CH_3)_3SiSi(CH_3)_3 \rightarrow 2(CH_3)_3Si^{\bullet}$$

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{e} 2(CH_3)_3Si^{+}$$

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{UV} 2(CH_3)_3Si^{\bullet} \quad (71\%)$$

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{UV} (CH_3)_3SiH + (CH_3)_2Si{=}CH_2 \quad (27\%)$$

Also the following reaction is likely to be significant,[23] since the HMDS precursor has a high hydrogen content:

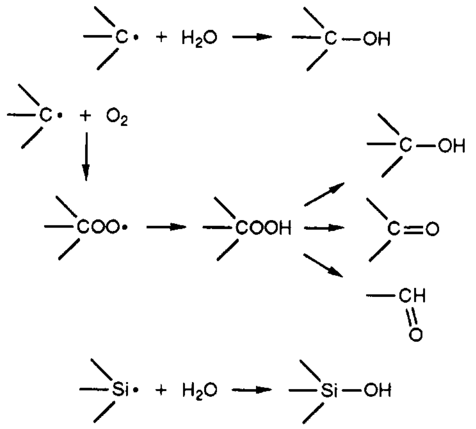
$$H^{\bullet} + (CH_3)_3SiSi(CH_3) \rightarrow (CH_3)_3SiH + (CH_3)_3Si^{\bullet}$$

All of these species can subsequently either undergo polymerization in the gas phase or react with free radical centers at the substrate surface. It is energetically favorable[20,24,25] for the cleavage of Si–Si (196 kJ mol^{-1}) bonds to form Si–C (291 kJ mol^{-1}) or Si–H (322 kJ mol^{-1}) linkages and also for the rupture of the Si–(CH$_3$)$_3$ bond to produce C–C (356 kJ mol^{-1}) and C–H (416 kJ mol^{-1}) connections, thereby resulting in an extended network.

It is quite common for the occurrence of high internal stress within plasma-deposited thin films;[26] this can result in flaking and therefore the production of a fine powder. However, low coverages of organosilicon deposit do adhere well to a polyethylene substrate.[27] This can be attributed to the greater flexibility of polyethylene with respect to glass; also, since it is already organic in nature, it will be much more compatible with the plasma deposit, i.e., the plasma polymer/polyethylene interface will bond more easily than its plasma polymer/glass counterpart.

Also under comparable experimental conditions, the plasma polymerization of hexamethyldisilane onto polyethylene film[27] gave a weaker FTIR Si–H stretch at 2104 cm^{-1}, whereas the Si–H band of the freshly deposited powder was much stronger in intensity. Therefore one can deduce that the bulk material has a greater Si–H content than the thin layer deposited onto a polyethylene substrate. The differences observed in Si–H groups between the polyethylene and glass substrates can be explained on the basis of the effective surface area available for the plasma/solid interaction. Since a powder would be expected to have a far higher surface area than a thin coating, then there will be greater opportunity for attachment of Me$_3$Si$^{\bullet}$ radicals to the surface and also for the incorporation of CH$_3$ groups into the plasma polymer, together with any Si–H bond formation.

Plasma polymers are widely recognized as comprising of highly cross-linked networks with trapped free radicals.[28] Si–O and C–O have bond dissociation energies of 531 and 340 kJ mol^{-1} respectively,[25] and therefore it is energetically favorable for trapped reactive centers to interact with oxygen and moisture from the air:[9]



Following ageing, the shift in the Si(2p) XPS peak to a higher binding energy, the increase in oxygen atomic percentage, the appearance of shoulders in both the C(1s) and Si(2p) regions, and the presence of O–H, CO$_x$, and Si–O related NMR/FTIR bands support this explanation.

The chemical nature of the as-collected bulk material and its subsequent ageing are similar in some respects to plasma-deposited thin films derived from tetramethylsilane[29] and vinyltrimethylsilane[30] precursors. For instance, comparable infrared absorption bands are reported, and subsequent reactions with oxygen and moisture cause the same types of oxygenated functionality to be incorporated. However the hexamethyldisilane precursor is found to be much more susceptible toward plasma polymerization; this is clearly evident from the high deposition rates obtained in our studies. Most plasma polymerization reactions are restricted to coating applications due to their low yield, whereas the high efficiency offered by the hexamethyldisilane monomer means that bulk plasma polymers may become exploited in their own right in the future.

Conclusions

It has been demonstrated that by careful choice of precursor and glow discharge parameters, bulk organosilicon materials can be synthesized via plasma polymerization. Hexamethyldisilane has proven to be a suitable monomer for this purpose due to the chromophoric character of its Si–Si bond. Reactive centers trapped within the plasma deposit are found to subsequently undergo cross-linking and oxidation during prolonged exposure to air.

Acknowledgment. J.L.C.F. thanks Brazil's Conselho Nacional de Desenvolvimento Científico e Tecnológico for financial support during the course of this work.

Registry No. Hexamethyldisilane (homopolymer), 61469-35-0.

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