PLASMA POLYMERIZATION OF HEXAMETHYLDISILANE AND TETRAMETHYLSILANE PRECURSORS

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ABSTRACT

Plasma polymerization of structurally related tetramethylsilane ($[CH_3]_4Si$) and hexamethyldisilane ($[CH_3]_3SiSi[CH_3]_3$) molecules result in extended organosilicon networks. The chromophoric $\geq$Si-Si$\leq$ bond present in hexamethyldisilane makes this precursor much more susceptible towards plasma polymerization. Greater energies are needed in the case of tetramethylsilane, which in turn leads to a higher density of unsaturated centres in the product material.

INTRODUCTION

Carbosilicon plasma polymers have many potential applications: biocompatibile coatings[1], integrated optical circuitry[2,3], semiconductor device fabrication[4], and as adhesion promoters between glass fibres and polymer matrices[5]. Silylmethyl groups $[CH_3]_xSi$ ($x = 1,2,3$), and weak Si-Si linkages are understood to play a key role during the plasma polymerization of organosilanes[6].

In this article, the low temperature glow discharge polymerization of tetramethylsilane ($Si[CH_3]_4$) and hexamethyldisilane ($[CH_3]_3Si-Si[CH_3]_3$) has been studied by XPS, FTIR, and solid state NMR.

EXPERIMENTAL

Tetramethylsilane (TMS, 99.9% Aldrich Chemicals) and hexamethyldisilane (HMDS, 98% Aldrich Chemicals) were further purified by multiple freeze-pump-thaw cycles. Two types of substrate were used: low density polyethylene film (LDPE, Metal Box) and glass slides. Both of these were rinsed in isopropyl alcohol, and dried prior to use.

Glow discharge experiments were carried out in a cylindrical glass reactor (4.5 cm diameter, 490 cm^3 volume, base pressure = 1 x 10^{-2} Torr) enclosed in a Faraday cage[7]. It was fitted with a monomer inlet, a Pirani pressure gauge, and a two-stage rotary pump attached to a liquid nitrogen cold trap. A 13.56 MHz radio frequency (RF) source was inductively coupled to the reactor via a matching network and a copper coil. Excitation powers lower than 5 Watts could be sustained by pulsing the glow discharge. The substrate position was fixed at 6.5 cm from the reactor inlet. In the case of bulk material studies, powdered deposit was collected from all parts of the reaction vessel.

Organosilicon monomer was introduced into the reaction chamber at 1 x 10^{-1} Torr pressure, and mass flow rates (F_M) of 3.6 x 10^{-8} kg/s and 4.3 x 10^{-8} kg/s for TMS and HMDS respectively (i.e. at least 99.3% of F_M is the organosilane precursor). After allowing 5 mins for purging, the glow discharge was ignited.

X-ray photoelectron spectra were acquired on a Kratos ES200 surface analysis instrument operating in the fixed retarding ratio (22:1) analyser mode. Magnesium K_α X-rays were used as the photoexcitation source with an electron take-off angle of 30° from the surface normal. All binding energies are referenced to the hydrocarbon ($-\underline{C}_xH_y-$) component at 285.0 eV. Instrumentally determined sensitivity factors for unit stoichiometry were taken as C(1s) : O(1s) : Si(2p) equals 1.00 : 0.55 : 1.05.

Infrared absorbance spectra of powdered material, and coated polyethylene film were collected on a FTIR Mattson Polaris instrument. Plasma polymer powder was mixed with dried potassium bromide, then pressed into a disc, and characterized using the transmission method. Treated polyethylene film was mounted onto a variable angle attenuated total reflection (ATR) cell fitted with a KRS-5 crystal.

Solid-state NMR spectra were taken on a Varian VXR-300 spectrometer equipped with a Doty Scientific magic-angle-spinning (MAS) probe. ^{29}Si and ^{13}C NMR signals were recorded at 59.6 MHz and 75.4 MHz respectively. In both cases, tetramethylsilane (TMS) was used as the chemical shift reference.

Elemental microanalysis was done on a Carlo Erba Elemental Analyser (model 1106). A Philips X-ray diffractometer (model PW1009/80) fitted with a CuKα (λ = 1.5443 Å) tube, and a Debye-Scherrer camera, was used to evaluate whether the collected plasma powder contained any crystalline character.

RESULTS

Short deposition times resulted in a uniform coating; however longer times (6 hours) produced a substantial amount of non-crystalline brown powder. The HMDS material changed to a yellow colour on standing in air, whereas its TMS counterpart retained its brown appearance. Elemental microanalysis of the collected plasma deposits (at maximum deposition rates) yielded H/C ratios of 1.9 and 2.3 for TMS and HMDS respectively.

X-ray photoelectron studies showed that the Si/C ratio of plasma polymerized organosilicon coatings drops with increasing W/F_m, Figure 1; this fall is much more pronounced for HMDS. The Si(2p) peak is centred on 100.7 ± 0.1 eV for the TMS plasma powder, whereas in the case of HMDS it is shifted to 101.2 ± 0.1 eV.

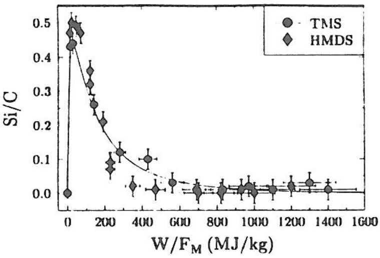

Figure 1 Si/C ratios as a function of glow discharge power: (a) TMS; and (b) HMDS.

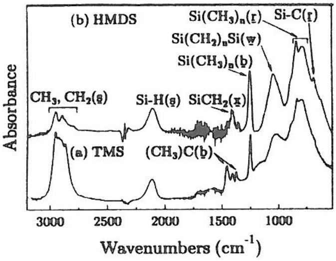

Figure 2 Transmission FTIR spectra of powdered plasma polymer: (a) TMS (W/F_m = 280 MJ/kg); and (b) HMDS (W/F_m = 120 MJ/kg). Stretching (s), rocking (r), bending (b), scissoring (x), and wagging (w).

ATR-FTIR studies were used to determine the optimum conditions for maximum deposition rate of organosilicon material onto polyethylene film. Greatest attenuation of the characteristic polyethylene bands was taken as corresponding to the thickest plasma polymer layer. It was deduced that carbosilane polymerization occurs most rapidly at W/F_m = 280 MJ/kg for TMS, and W/F_m = 120 MJ/kg for HMDS. FTIR transmission spectra of powdered material obtained from plasma polymerization of TMS and HMDS (at maximum deposition rates) are compared in Figure 2. The 2951 and 2895 cm^{-1} bands seen in the FTIR spectra of the freshly deposited powders arise from the overlap between CH_3 and CH_2 stretching frequencies. CH_3-C linkages can also be identified by peaks at 1460 cm^{-1} (methyl asymmetric bending in CH_3-C), and 1375 cm^{-1} (methyl symmetric bending in CH_3-C). Silicon related infrared absorptions are assignable as follows[8-11]: 2110 cm^{-1} (Si-H stretching), 1408 cm^{-1} (CH_2 symmetrical scissoring in Si-CH_2), 1250 cm^{-1} (CH_3 symmetric bending in Si$[CH_3]_n$), 1026 cm^{-1} (Si-O-Si and/or Si-O-C asymmetric stretching and/or CH_2 wagging in Si-$[CH_2]_n$-Si), 833 cm^{-1} (CH_3 rocking in Si$[CH_3]_n$, n = 2, 3), 791 cm^{-1} (CH_3 rocking in Si$[CH_3]_n$, n = 1, 2), and 685 cm^{-1} (Si-C stretching). Clearly, HMDS gives rise to a silicon-rich plasma polymer, consisting of mainly Si-CH_2, Si-$(CH_2)_n$-Si, and Si$(CH_3)_n$ moieties; whereas the TMS product contains a greater organic content.

^{13}C and ^{29}Si solid state NMR spectra of freshly deposited TMS and HMDS plasma polymers are shown in Figure 3. The most intense ^{13}C and ^{29}Si NMR signals are located at around 0 ppm, which implies that the major chemical environment present in these plasma deposits is very similar to that found in the TMS reference compound (i.e. Si$[CH_3]_n$)[12-14].

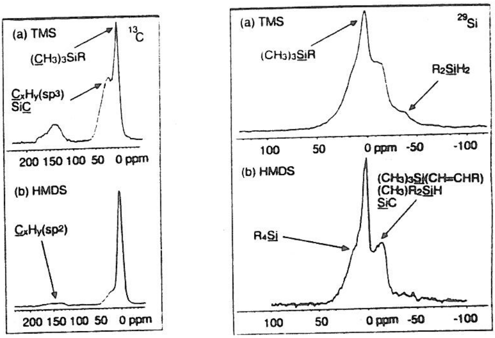

Figure 3 ^{13}C and ^{29}Si NMR spectra of powdered glow discharge deposit: (a) TMS (W/F_m = 280 MJ/kg); and (b) HMDS (W/F_m = 120 MJ/kg).

The shoulder at approximately 20-50 ppm in the ^{13}C NMR spectra, is characteristic of either sp^3 carbon atoms located within a hydrocarbon chain, or silicon carbide species[15]; clearly this feature is much more intense for the TMS product, which would be consistent with it having a greater organic content. Unsaturated centres are evident in the 120 - 180 ppm range; there appears to be a higher concentration of unsaturated carbon linkages in the TMS plasma polymer.

The ^{29}Si NMR peak at 6 ppm is most likely to be silicon centres fixed to hydrocarbon chains, of the type R_4Si, where not more than one R chain is a methyl group. The peak at approximately -11 to -14 ppm can be attributed to one or more of the following: silicon centres with unsaturated carbon centres attached to the β position from the $[CH_3]_3Si$ group of the type $[CH_3]_3Si[CH{=}CHR]$ where R = H, CH_3, or $Si[CH_3]_3$; or $[CH_3]R_2SiH$, provided R has an alkyl chain containing at least two $[-CH_2-]$ linkages; or perhaps silicon carbide type species[15]. The weak feature at -35.0 ppm is most likely to be some kind of $R^1R^2SiH_2$ linkage. The ^{29}Si NMR results are consistent with ^{13}C NMR experiments: TMS plasma polymer has a higher organic content, and contains a greater number of unsaturated carbon centres.

DISCUSSION

XPS, FTIR, and solid state NMR measurements show that $(CH_3)_nSi$ linkages are the major functionalities for both plasma polymers. It can also be concluded from XPS and FTIR, that the TMS product contains a higher proportion of organic species.

The brown appearance of freshly deposited glow discharge polymerization products is indicative of unsaturated centres. The fact that HMDS plasma polymer discolours with time, whereas its TMS counterpart remains brown and possesses a smaller H/C elemental ratio, is consistent with the latter material containing a larger fraction of sp^2 carbon centres. The lower Si(2p) XPS binding energy value for the TMS plasma polymer can be explained in terms of this material being effectively electron-rich in light of its unsaturated character. Solid state NMR experiments are consistent with the aforementioned description, since the ^{13}C sp^2 and the ^{29}Si $[CH_3]_3Si[CH=CHR]$ environments are of greater intensity for the TMS experiments.

The only structural difference between the TMS and HMDS precursors is the Si-Si linkage contained in the latter molecule. The greater reactivity of the HMDS monomer must therefore arise from its chromophoric Si-Si linkage. Electron-molecule[15] and photon-molecule[16] reactions are likely to be two of the key processes responsible for ionization and dissociation within the HMDS glow discharge:

$$(CH_3)_3SiSi(CH_3)_3 \text{ ---e----> } 2(CH_3)_3Si^+$$

$$(CH_3)_3SiSi(CH_3)_3 \text{ ---uv---> } 2(CH_3)_3Si\cdot \qquad (71\%)$$

$$(CH_3)_3SiSi(CH_3)_3 \text{ ---uv---> } (CH_3)_3SiH + (CH_3)_2Si{=}CH_2 \qquad (27\%)$$

Whereas for TMS, plasma polymerization will only occur after a number of fragmentation and rearrangement steps. Hence the prerequisite for higher glow discharge energies in this case. Extensive breakdown of the incoming precursor, and greater sputtering of the growing plasma polymer are more likely to generate unsaturated linkages.

CONCLUSIONS

Low temperature glow discharge polymerization of the structurally related TMS and HMDS molecules results in an extended network of $-[C_xH_y]_nSi-$ linkages. TMS plasma polymer contains a higher proportion of organic entities, and possesses a significant degree of unsaturation. Whereas, the HMDS derived material has a greater number of $-[CH_3]_nSi-$ linkages.

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