

Plasma Polymerization of Hexamethyldisilane onto Polyethylene Film

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Received September 10, 1991; Revised Manuscript Received May 5, 1992

ABSTRACT: Polyethylene film has been coated with a plasma polymer derived from hexamethyldisilane ($[\text{CH}_3]_3\text{SiSi}[\text{CH}_3]_3$). The extent of Si incorporation into the organosilicon overlayer was determined by XPS, and the corresponding molecular structure was elucidated by ATR-FTIR spectroscopy. Glow discharge power and substrate position are found to strongly influence the deposition rate and the chemical nature of the modified polyethylene substrate.

Introduction

Plasma polymerization is poorly understood at the molecular level in comparison to conventional radical or ionic polymerization.¹ Molecules injected into a glow discharge are liable to undergo activation and fragmentation via interactions with the inherent electrons, radicals, ions, and photons of a plasma. Under the optimum conditions, successive dissociation and recombination processes within a plasma can yield extended molecules in the vapor phase and may concurrently lead to molecular fragments becoming attached to a local substrate.

Organosilicon plasma polymers are widely reported to possess high dielectric strengths,² have desirable gas separation characteristics,³ and exhibit good adhesion to conventional polymers.⁴ Reactive silylmethyl groups are believed to be mainly responsible for any cross-linking processes which may occur during the plasma polymerization of organosilanes.⁵ Tetramethylsilane ($\text{Si}[\text{CH}_3]_4$),^{6,7} phenylsilane ($[\text{C}_6\text{H}_5]\text{SiH}_3$),⁸ and trimethylvinylsilane ($[\text{CH}_3]_3\text{Si}[\text{CHCH}_2]$)⁴ are amongst the carbosilane monomers previously used. In this study we selected hexamethyldisilane ($[\text{CH}_3]_3\text{SiSi}[\text{CH}_3]_3$) as the precursor. This monomer contains a weak Si-Si linkage, which should make it much more susceptible toward plasma polymerization than that found for comparable monosilicon-containing precursors.

Experimental Section

Hexamethyldisilane (98%; Aldrich Chemical Co.) was used for the plasma-assisted deposition experiments. Prior to its use, the precursor was transferred under a nitrogen atmosphere into a monomer reservoir and then subjected to multiple freeze-pump-thaw cycles. Polyethylene film (LDPE; Metal Box Co.) was rinsed in isopropyl alcohol and subsequently dried in a vacuum desiccator.

The electrodeless flow reactor used in this study is similar to that previously described by Shard et al.⁹ It was fitted with a monomer inlet, a Pirani pressure gauge, a 47 L min⁻¹ two-stage rotary pump with a liquid-nitrogen cold trap, and a matching network for inductive coupling of a 13.56-MHz radio-frequency source. All joints were grease-free. Radio-frequency coils extended along 11–19 cm from the precursor inlet. Clean polyethylene film was placed onto a glass slide and inserted horizontally into the reactor. For experiments concerned with evaluating the influence of power and time, the polymer substrate was positioned 6.5 cm downstream from the monomer inlet. Prior to each run, the reactor was washed with detergent, then dried in an oven at 140 °C, and finally cleaned with a high-power (50-W) air glow discharge.

First of all, the system was pumped down to 2×10^{-2} Torr, and the walls of the reactor were allowed to outgas. The leak rate was calculated¹⁰ to be 2.6×10^{-10} kg/s (the molecular composition of air being 79% N₂ and 21% O₂). Hexamethyldisilane was introduced into the reaction vessel at a pressure of 1×10^{-1} Torr, with a mass flow rate (F_m) of 4.3×10^{-8} kg/s. This implies that the organosilane precursor accounts for at least 99.4 % of the gaseous contents in the reaction chamber. The plasma was ignited 5 min after the introduction of monomer. On termination of plasma-assisted deposition, the system was evacuated down to 2×10^{-2} Torr for 5 min (this was done as a precaution against any remaining precursor undergoing hydrolysis following exposure to air and subsequently condensing onto the substrate surface).

Thin-film deposition was studied as a function of power ranging from 0.5 to 50 W. Continuous plasmas were used over the 2–50-W range and pulsed plasmas from 0.5 to 4 W. The pulsed mode gave greater stability to the glow discharge at low powers¹¹ (the pulse duration of a 5-W plasma was adjusted in order to obtain a lower mean power). Overlap in the 2–4-W regime was used as a check to ensure that the two methods were consistent.

X-ray photoelectron spectra were acquired on a Kratos ES200 surface analysis instrument. Mg K α radiation 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 take-off angle of 30° from the surface normal. No radiation damage to the substrate was observed over the typical time scale involved in these measurements. Data accumulation and component peak analysis were performed with an IBM PC computer, using linear background subtraction and gaussian fits having fixed fwhm. All binding energies are referenced to the hydrocarbon component at 285.0 eV.¹² 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.

Infrared absorbance spectra were taken on a FTIR Mattson Polaris instrument, using a variable-angle ATR cell fitted with a KRS-5 crystal. Typically, 100 scans were recorded at a resolution of 4 cm⁻¹, with an incident beam angle of 45° (resulting in 14 internal reflections).¹³

Results

X-ray Photoelectron Spectroscopy. The surface composition of the polyethylene substrate following plasma modification was determined by XPS analysis. Figures 1 and 2 show the XPS spectra of the C(1s) and Si(2p) regions, respectively, of polyethylene film before and after a hexamethyldisilane glow discharge treatment at 5 W for 10 min. A small amount of oxygen (~3% at a O(1s) binding energy of 532.8 eV) was always found in the freshly deposited plasma coating. Variable take-off angle studies reveal that this is localized at the surface. This probably originates from the reaction of trapped free radicals in the

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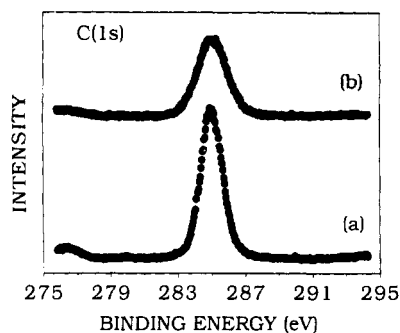


Figure 1. C(1s) XPS spectra of (a) clean polyethylene and (b) following exposure of polyethylene film to a 5-W plasma of hexamethyldisilane (10 min and 6.5 cm from inlet).

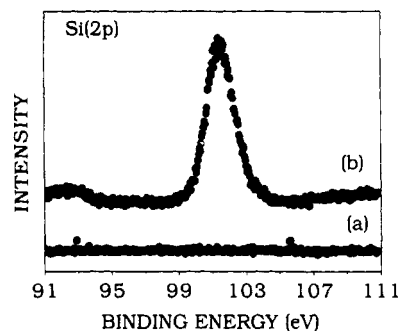


Figure 2. Si(2p) XPS spectra of (a) clean polyethylene and (b) following exposure of polyethylene film to a 5-W plasma of hexamethyldisilane (10 min and 6.5 cm from inlet).

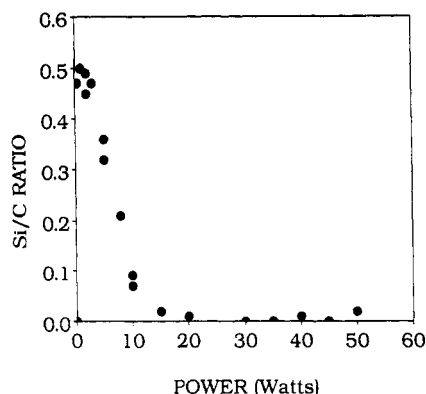


Figure 3. Si/C ratio as a function of glow discharge power (10 min and 6.5 cm from inlet).

deposited coating with moisture and oxygen in the air during transport of the specimen from the reactor to the XPS spectrometer. The main C(1s) peak has been referenced to 285.0 eV, which corresponds to the presence of C-C, C-H, and C-Si bonds.^{14,15} Only one symmetrical feature was observed in the Si(2p) region at a binding energy of 101.3 eV; this can be associated with Si-C and Si-H environments.^{7,14,15}

Figure 3 summarizes the variation of the Si/C ratio as a function of plasma power; it can be seen that the relative amount of silicon falls off continually with increasing wattage. Also the dependence of the Si/C ratio on the position of the substrate within the reactor is described in Figure 4 (5 W, 10 min). The amount of silicon incorporated into the deposited layer drops on moving downstream from the monomer inlet. Figure 5 illustrates the relationship between time and the Si/C ratio at a plasma power of 5 W. It can be seen that the Si/C value does not vary significantly (this is within experimental error of the data analysis). Therefore, the deposition process must quickly reach a steady state.

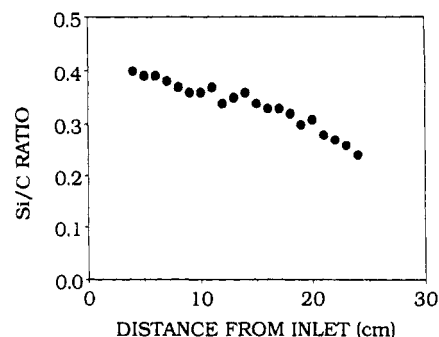


Figure 4. Dependence of the Si/C ratio on the distance of the polyethylene substrate from the precursor inlet (5 W and 10 min).

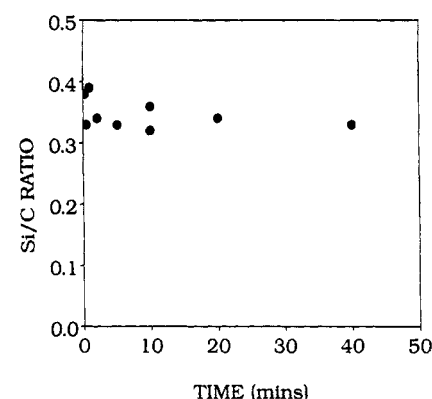


Figure 5. Relationship between the Si/C ratio of the deposited film and time of plasma polymerization (5 W and 6.5 cm from inlet).

ATR Infrared Spectroscopy. Infrared spectra of clean polyethylene and also polymer substrates which have been exposed to a range of hexamethyldisilane glow discharges are collated in Figure 6. According to the literature, the characteristic absorption bands of clean polyethylene film can be assigned as follows:^{16,17} 2915 (antisymmetrical C-H stretching in CH₂), 2847 (symmetrical C-H stretching in CH₂), 1472 (CH₂ bending), 1462 (CH₂ bending), 1366 (CH₂ wagging and/or symmetrical CH₃ movements), 729 (CH₂ rocking; this is dependent upon the crystallinity¹⁸ and orientation¹⁹ of the polyethylene), and 720 cm⁻¹ (mainly CH₂ rocking from the amorphous regions, with a minor contribution from crystal field splitting¹⁸).

Assignment of the infrared absorption bands observed for the plasma polymers deposited onto polyethylene film is presented in Figure 7. Most of these peaks are similar to those reported previously for plasma polymers derived from related carbosilane precursors.^{10,20-22} They include the following: 2118 (stretching in Si-H), 1250 (CH₃ symmetrical bending, in Si(CH₃)_n), 1036 (Si-O-Si and/or Si-O-C, and/or CH₂ wagging in Si(CH₂)_nSi), 833 (CH₃ rocking in Si(CH₃)_n, *n* = 2 and 3), 791 (CH₃ rocking in Si(CH₃)_n, *n* = 1 and 2), 689 cm⁻¹ (Si-C stretching). An additional weak absorption band at 621 cm⁻¹ was found for the coating obtained from the 2-W glow discharge; this can be attributed to the presence of vinyl groups.²³

At low plasma powers, there is a small occurrence of vinyl groups, which is accompanied by a considerable number of silicon-related groups: Si(CH₂)_nSi, Si(CH₃)_n, and probably a minor fraction of Si-O-Si and/or Si-O-C originating from the reaction of trapped free radicals with oxygen and moisture in the air during sample transfer. With increasing power, the vinyl component gradually disappears, together with the groups associated with silicon, until the infrared spectrum corresponds to virtually

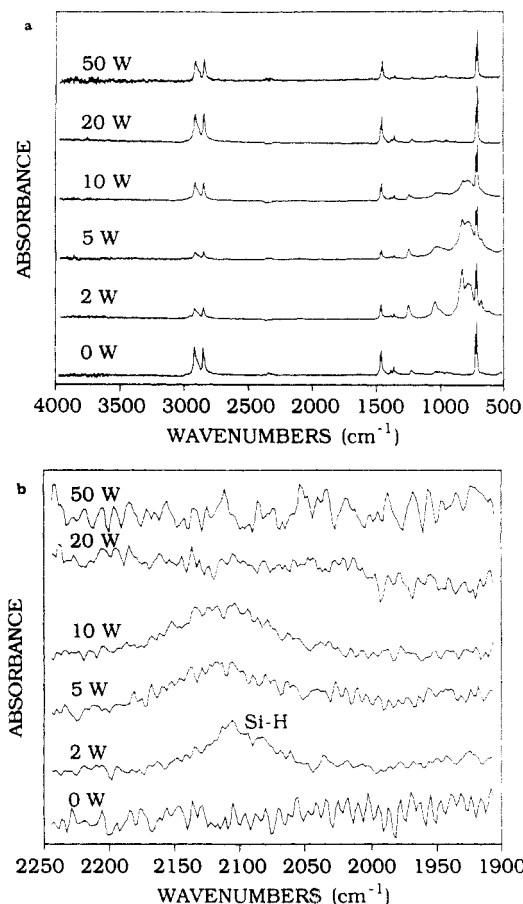


Figure 6. (a) ATR infrared spectra as a function of plasma power (10 min and 6.5 cm from inlet). (b) Expanded Si-H stretching region (10 min and 6.5 cm from inlet).

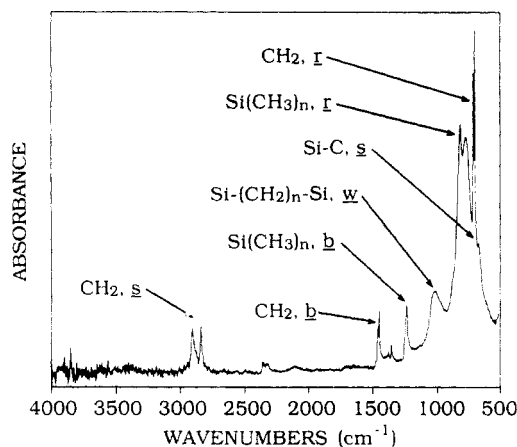


Figure 7. Assignment of the infrared stretches for the plasma-deposited coating: stretching (s), rocking (r), bending (b), and wagging (w); (5 W, 10 min, and 6.5 cm from inlet).

that of clean polyethylene (20 and 50 W). It should be noted that, as the power increases, the proportion of methyl groups linked to silicon decrease: at 2 W, the absorption of the 833-cm^{-1} band (CH_3 rocking in $\text{Si}(\text{CH}_3)_n$, $n = 2$ and 3) is much greater than that at 791 cm^{-1} (CH_3 rocking in $\text{Si}(\text{CH}_3)_n$, $n = 1$ and 2), whereas these bands are of roughly the same intensity at 10 W.

The minimal absorbance intensity of the characteristic polyethylene features at 2915 and 2847 cm^{-1} occurs at approximately 5 W. This correlates to the highest deposition rate of Si-containing material observed in the XPS measurements. Since the sampling depth is inversely proportional to the infrared wavenumber, these bands are expected to be more surface sensitive than the other characteristic polyethylene features found at lower wave-

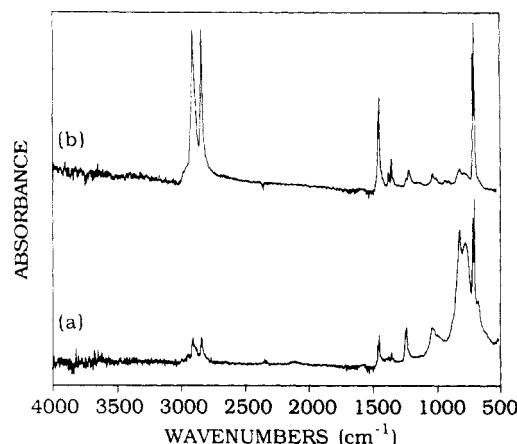


Figure 8. Infrared spectra of the plasma-treated polyethylene film at (a) 4 cm and (b) 24 cm from the precursor inlet (5 W and 10 min).

numbers. Any incorporation of plasma polymer into the polyethylene substrate could also contribute to this differential attenuation of polyethylene infrared features. This would be consistent with the observation that these infrared spectra are markedly different compared to those obtained for the bulk plasma polymer material²⁴ (where the C-H stretching region for CH_2 has extra components associated with C-H stretches from CH_3 groups at 2962 and 2872 cm^{-1}).

At high powers (50 W), the methyl band at 1366 cm^{-1} is of lower intensity than that seen for clean polyethylene, this implies a deficiency of methyl end groups at the substrate surface. The absorbance ratio of the strong 729 - and 720-cm^{-1} components of the methylene rocking doublet gives an indication of the relative changes in crystallinity and/or orientation at the polyethylene surface. On raising the plasma power, the polyethylene becomes more amorphous and/or disorientated in the vicinity of the substrate-plasma polymer interface.

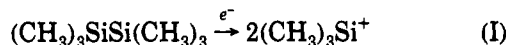
Figure 8 shows the infrared spectra of 5-W treated polyethylene film which was located at different positions within the flow discharge (4 and 24 cm away from the monomer inlet). Deposition of a Si-containing plasma polymer is greatest near the reactor inlet, since all the bands related to this material are more pronounced in this region.

Discussion

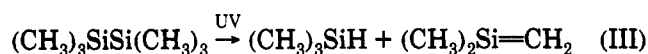
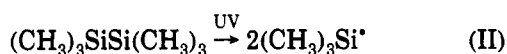
Very complex physicochemical processes are understood to occur during plasma-assisted deposition. These include fragmentation and recombination of parent molecules, the generation of both positive and negative ions, atoms, and electrons, and a broad electromagnetic spectrum.²⁵ Plasma polymerization is known to be dependent upon a composite parameter W/F_m (where W is the discharge power, and F_m is the monomer mass flow rate).¹⁰ For low values of this parameter, the chemical nature of the deposited material is strongly dependent upon the structural features of the monomer. At high W/F_m values, the majority of the precursor molecules polymerize via an atomic polymerization mechanism, and thereby the composition of the monomer rather than its molecular structure has a substantial influence on the resulting polymeric layer. In these experiments, powers ranging from 0.5 to 50 W correspond to W/F_m ratios of between 1.2×10^7 and $1.2 \times 10^9\text{ J kg}^{-1}$. Low powers (or W/F_m values) are required in order to limit the extent of fragmentation of gaseous species and any accompanying ablation of deposited material. Plasma polymerization can become even more

favorable if the cleavage of weak bonds in the precursor leads to the formation of stronger bonds in the plasma polymer.

The dependence of plasma polymerization of hexamethyldisilane upon the various experimental parameters investigated in this study can be accounted for on the basis of the relative bond strengths associated with the precursor molecule.^{26,27} H-C = 415 kJ mol⁻¹, Si-C = 291 kJ mol⁻¹, Si-Si = 196 kJ mol⁻¹. Electron-molecule and photon-molecule reactions are known to be two of the key processes responsible for ionization and dissociation within the glow discharge. Electron impact²⁸ and surface ionization²⁹ mass spectrometry studies of hexamethyldisilane have shown that the major ion is (CH₃)₃Si⁺:



Vacuum-ultraviolet radiation is known to be a major component of a glow discharge.³⁰ Photolysis of hexamethyldisilane at 206 nm proceeds via two major decomposition channels: Si-Si bond rupture yielding trimethylsilyl radicals (71 %) and the molecular elimination of dimethyldisilene (27 %):³¹



All of these species (I-III) either can subsequently undergo polymerization in the gas phase or react with free-radical centers at the substrate surface. Cleavage of the Si-Si bond in hexamethyldisilane to form Si-C or Si-H (Si-H = 321 kJ mol⁻¹)²⁷ linkages and rupture of the Si-(CH₃) bond to produce C-C (C-C = 356 kJ mol⁻¹)³² connections, hence creating a polymeric framework, are both energetically desirable. Formation of C-C bonds is a key step in plasma polymerization.³³ Such low levels of W/F_m required for film deposition have also been reported for other carbosilane precursors.^{4,6} A reduction in the number of methyl groups attached to silicon with an increase in plasma power is consistent with a greater degree of fragmentation. The high deposition rate of Si-based moieties toward the reactor inlet is further evidence for the vulnerability of the organosilane molecule in the vicinity of a glow discharge.

At higher powers (>20 W), the absence of Si or Si-containing groups can be attributed to two factors: To some extent, deposition of material was occurring within the tubulation which links the inlet of the reactor to the monomer reservoir; plasma polymer could be visually seen in this tubulation at powers greater than 15 W. Also, at such high powers, there is a greater degree of fragmentation and production of energetically excited gaseous species which may participate in substrate ablation and cross-linking, with the accompanying departure of stable organosilicon species via the reactor outlet. This accounts for the deficiency of methyl end groups at the surface following a 50-W plasma treatment and also the highly amorphous and/or disorientated nature of the resulting polyethylene surface.

Finally, these plasma polymer coatings were found to be very tough and adhered extremely well to the polyethylene substrate. Such laminates could find applications as scratch-resistant coatings.

Conclusions

Plasma polymerization of hexamethyldisilane onto polyethylene is greatest at low powers. Under these

conditions, relatively little ablation of deposited material takes place. Rupture of the weak Si-Si and C-Si bonds in the precursor is energetically favored, thereby generating reactive species which can readily undergo recombination in the gas phase, and cross-linking with free-radical centers at the substrate surface to produce an extended molecular network. The resulting top layer examined in this study has been found to be chemically different from the corresponding bulk plasma polymer, in that it consists of organosilicon polymer embedded into amorphous and/or disorientated polyethylene film. At higher plasma powers, ablation and deposition further upstream in the reactor tend to predominate.

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

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