Atmospheric Pressure Glow Discharge Deposition of Polysiloxane and SiOx Films

L. J. Ward, W. C. E. Schofield, and J. P. S. Badyal*

Department of Chemistry, Science Laboratories, Durham University, Durham DH1 3LE, England, U.K.

A. J. Goodwin
Dow Corning Ltd., Barry CF63 2YL, Wales, U.K.

P. J. Merlin
Dow Corning SA, Parc Industriel, 7180 Seneffe, Belgium

Received May 7, 2002. In Final Form: December 13, 2002

Hydrophilic polysiloxane-like thin films have been deposited onto polyethylene by introducing octamethylcyclotetrasiloxane and tetramethylcyclotetrasiloxane precursors through an ultrasonic atomizer into an atmospheric pressure glow discharge. Enrichment of the gas feed with oxygen gives rise to the formation of hydrophilic SiOx coatings which exhibit an improvement in gas barrier.

Introduction

Silicon-containing films find many technological applications: these include the packaging,1-8 biomedical,9,10 automotive,11-13 and microelectronics14-16 industries. Chemical vapor deposition (CVD)17 and the pyrolytic degradation of silicon-containing precursors are often used in this context. However, the inherently high temperatures (typically over 400 °C) make these techniques unsuitable for treating temperature-sensitive materials, such as polymers and semiconductors17 (e.g., GaAs, InP, and a-Si: H). One common approach employed to overcome this limitation has been to use low pressure glow discharge methods such as plasma enhanced CVD (PECVD)18,19 and remote plasma enhanced CVD (RPECVD).20,21 The prerequisite vacuum necessary for these processes makes them expensive and limited to batch treatments. UV irradiation22 and UV/ozone23 treatment are viable alternatives capable of operating at atmospheric pressure and low temperature; however, film growth typically tends to be slow.

In this article, an atmospheric pressure glow discharge (APGD) fitted with an ultrasonic atomizer is used to deposit polysiloxane and silicon oxide coatings at high growth rates. APGD plasmas typically use a helium diluent and a high frequency (>1 kHz) power supply to generate a homogeneous glow discharge at atmospheric pressure via a Penning ionization mechanism.24-27 These plasmas are highly uniform in nature compared to other types of nonequilibrium atmospheric plasma (such as coronas or dielectric barrier discharges, where the reactive species tend to be concentrated into narrow filaments and therefore can cause localized surface damage and degradation28,29). Octamethylcyclotetrasiloxane (OMCTS) and tetramethylcyclotetrasiloxane (TMCTS) have been chosen as precursors in the present study, since they consist of cyclic Si–O structures, which can potentially ring open in the plasma. After decomposing in the plasma, the hydroxyl-terminated radicals derived from these polymers can be incorporated into the deposited film, which is further cross-linked by an ultrasonic atomizer. This results in a highly cross-linked hydrophilic polysiloxane network, which can potentially enhance its properties. The deposition of polysiloxane networks; see structures 1 and 2. Infrared spectroscopy (ATR-FTIR), contact-angle, solid
ultrasonic power supply

syringe-pump

nozzle

earth electrode

droplets

sample

glass dielectric

Figure 1. Schematic of the APGD deposition reactor.

APGD Deposition of Polysiloxane and SiO$_x$ Films


Chart 1

Structure 1 Octamethylcyclotetrasiloxane (OMCTS)

Structure 2 Tetramethylcyclotetrasiloxane (TMCTS)

Experimental Section

The home-built atmospheric pressure glow discharge (APGD) deposition reactor constituted a high voltage 15 kHz ac power supply applied across two aluminum electrodes spaced 12 mm apart, with the lower live electrode shielded by a glass dielectric plate; see Figure 1. An ultrasonic nozzle (Sono-tek, 8700-120) was embedded flush within the upper, earthed electrode and powered by a broad-band ultrasonic generator (Sono-tek, 06-05108). This employs a piezoelectric transducer to convert liquid feed into an atomized spray (in principle permitting the rapid vaporization of even nonvolatile precursors). Octamethylcyclotetrasiloxane (OMCTS; Fluka 99%) and tetramethylcyclotetrasiloxane (TMCTS; Fluorochem 95% minimum) were introduced into the ultrasonic nozzle using a syringe pump at a flow of 0.12 mL/h. When the liquid mixture was pumped off by placing the samples under a pressure of 1020 mbar. Two compositions were used: helium (BOC, 99.99%) and a 99% helium/1% oxygen (BOC, 99.998%) process gas was then admitted at a flow rate of 1900 sccm and a pressure of 10 Torr.

Plasma deposition entailed placing a piece of polyethylene film substrate (ultrasonically washed for 30 s in a 1:1 mixture of deionized water and gas permeation measurements.

Gas permeation measurements were acquired using a mass spectrometric device. This comprised inserting the coated polyethylene substrate between two drilled-out stainless steel flanges and a viton gasket. This assembly was attached to a UHV ion gauge (Vacuum Generators, VIG 24) and a quadrupole mass spectrometer (Vacuum Generators, SX200) interfaced to a PC computer were used to monitor the permeant pressure drop across the 30° from the substrate normal. Instrumentally determined sensitivity factors were taken as C(1s):O(1s):Si(2p) = 1.00:0.57:0.72. Sample charging was taken into consideration by referencing all spectra relative to the C(1s) hydrocarbon peak at 285.0 eV. The oxidation state of silicon centers was estimated using Gaussian peak shapes to fit the Si(2p) envelope. The Si–O peak position was set at 102.0 eV, Si–O$_2$ at 103.0 eV, and Si–O$_3$ at 104.0 eV. The total amount of siliceous material (SiO$_x$) was then calculated by summing the amount of silicon and oxygen in the Si–O$_x$, Si–O$_2$, and Si–O$_3$ environments.

ATR–FTIR spectra of the deposited films were recorded using 100 scans at 4 cm$^{-1}$ resolution on a Mattson Polaris spectrometer fitted with an attenuated total reflectance (ATR) accessory (Graseby Specac Golden Gate).

A spectrophotometer (Aquila Instruments, nkd-6000) was used to determine film thickness. Transmittance–reflection curves over the 350–1000 nm range were fitted to a Drude–Lorentz model using a modified Levenburg–Marquardt procedure. Repeatability and sample homogeneity were assessed by recording multiple readings from several different samples.

Contact angle values were obtained with a video capture apparatus (AST Products VCA2500XE) using sessile 2 μL droplets of deionized water.

Solid state NMR spectroscopic analysis was performed upon coatings scraped from the glass dielectric and packed into a 6 mm rotor. $^{29}$Si NMR spectra were acquired at 79.4 MHz with a gated decoupling sequence on a JEOL Lambda 400 MHz spectrometer, using magic angle spinning (MAS) at 5 kHz and a pulse delay time of 3 s. Under these conditions, analysis is considered to be semiquantitative. Octakistrimethylsilyloxysiloxane (Dow Corning) was used as an external reference.

Gas permeation measurements were acquired using a mass spectrometric device. This comprised inserting the coated polyethylene substrate between two drilled-out stainless steel flanges and a viton gasket. This assembly was attached to a high vacuum (UHV) chamber via a gate valve (base pressure of 5 × 10$^{-10}$ Torr) with the coated side of the polymer film exposed to an oxygen (BOC, 99.998%) pressure of 1000 Torr. A UHV ion gauge (Vacuum Generators, VIG 24) and a quadrupole mass spectrometer (Vacuum Generators, SX200) interfaced to a PC computer were used to monitor the permeant pressure drop across

(30) Ultrasonic-nozzle Product Information, Sono-tek, U.S.A.


(35) Technical Information, Aquila Instruments, Cambridge, UK.
Table 1. Summary of XPS, Contact Angle, and Deposition Rate Measurements

<table>
<thead>
<tr>
<th>sample</th>
<th>% C</th>
<th>% O</th>
<th>% Si</th>
<th>% SiO$_{x-y}$</th>
<th>contact angle (deg)</th>
<th>deposition rate (nm min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMCTS, theoretical monomer</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>0</td>
<td>107.8 ± 9.2$^a$</td>
<td>28 ± 4</td>
</tr>
<tr>
<td>OMCTS, 100% He</td>
<td>43.3 ± 2.5</td>
<td>29.3 ± 0.8</td>
<td>25.8 ± 0.6</td>
<td>35.7 ± 6.5</td>
<td>107.8 ± 9.2$^a$</td>
<td>28 ± 4</td>
</tr>
<tr>
<td>OMCTS, 99% He, 1% O$_2$</td>
<td>25.5 ± 5.2</td>
<td>48.5 ± 4.5</td>
<td>26.0 ± 0.7</td>
<td>74.4 ± 2.8</td>
<td>56.4 ± 9.8</td>
<td>29 ± 4</td>
</tr>
<tr>
<td>TMCTS, theoretical monomer</td>
<td>33.3</td>
<td>33.3</td>
<td>33.3</td>
<td>0</td>
<td>102.3 ± 2.8</td>
<td>82 ± 11</td>
</tr>
<tr>
<td>TMCTS, 100% He</td>
<td>32.5 ± 0.3</td>
<td>39.1 ± 1.0</td>
<td>28.4 ± 0.6</td>
<td>65.4 ± 1.3</td>
<td>102.3 ± 2.8</td>
<td>82 ± 11</td>
</tr>
<tr>
<td>TMCTS, 99% He, 1% O$_2$</td>
<td>9.2 ± 0.2</td>
<td>61.4 ± 2.2</td>
<td>29.5 ± 2.0</td>
<td>81.5 ± 5.9</td>
<td>102.3 ± 2.8</td>
<td>82 ± 11</td>
</tr>
</tbody>
</table>

$^a$ Clean polyethylene has a contact angle of 105.8 ± 1.5°.

Figure 2. Si(2p) XPS spectra of octamethylcyclotetrasiloxane films deposited in (a) helium APGD and (b) helium/oxygen APGD.

Results

(a) Octamethylcyclotetrasiloxane Deposition.

APGD deposition of OMCTS in the presence of helium carrier gas yielded hydrophobic coatings with surface elemental abundances resembling those of the monomer; see Table 1. Mixing oxygen with the helium feed gas produced a hydrophilic (low contact angle), oxidized surface containing a reduced amount of carbon. A corresponding increase in the Si(2p) binding energy intimated the formation of a more inorganic, SiO$_x$-rich environment, see Figure 2. Spectrophotometric thickness measurements indicated that the films deposited in pure He and the He/O$_2$ mixture were 279 ± 36 and 286 ± 38 nm thick, respectively; see Table 1.

ATR–FTIR spectra of (a) polyethylene substrate, (b) octamethylcyclotetrasiloxane liquid, (c) helium APGD deposited octamethylcyclotetrasiloxane, and (d) helium/oxygen APGD deposited octamethylcyclotetrasiloxane.

bulk chemical structure of the coating (whereas XPS is only sensitive to the outermost 2–5 nm). Films deposited on polyethylene substrates using an OMCTS/He APGD displayed many IR spectral features similar to those seen for the liquid OMCTS precursor; see Figure 3. The main differences were an enhancement of the peak at ~850 cm$^{-1}$ and the emergence of a shoulder on the band at 1100–1000 cm$^{-1}$ (Si–O–Si stretch). The precise nature of the polymerized product is difficult to determine since absorbances due to Si–CH$_2$, Si–O–C and Si–O–Si (1020–1090 cm$^{-1}$) and Si–O–Si, Si–C, Si–H, and Si–Me features all overlap in the 880–800 cm$^{-1}$ region. The absence of polyethylene bands at 1450, 2850, and 2950 cm$^{-1}$ indicated that the deposited films were sufficiently thick to preclude infrared sampling of the underlying substrate.

OMCTS coatings deposited in the presence of a helium/oxygen mixture exhibited several new infrared spectral features; see Figure 3. The Si–O–Si stretching vibrations (1100–1000 cm$^{-1}$) broadened and shifted toward higher wavenumber.
absorbed H2O, respectively.18,20,46,47 The absence of the precursor, especially in the presence of He/O2, where deposition rates were also much greater for the TMCTS several micron-thick films were grown.

The broadening of the Si monomer; see Figure 6. The main differences were a broadening of the Si–O–Si stretch (1100–1000 cm−1) and this can be taken as being representative of quartz-like material.23 In contrast, the Si–Me band at 1260 cm−1 became attenuated, intimating the oxidative removal of methyl groups.13,22 Bands at ~910 and 3500–3000 cm−1 also emerged, indicative of Si–OH and SiOH–H2O/absorbed H2O2, respectively.18,20,46,47 The absence of the C–H stretch at 2950 cm−1 48 (a band seen for both liquid OMCTS and the helium deposited polymer) provided evidence to support the preferential loss of organic material.

29Si solid state NMR analysis of the material deposited in helium showed predominantly (Me2SiO)1/2, at a chemical shift of approximately −20 ppm, indicative of a polysiloxane polymer and any entrapped OMCTS monomer; see Figure 4. The signal at −67 ppm is due to MeSiO3/2 signifying the presence of some cross-linking or branching. The small signals at −8.9 and −58.5 ppm were attributed to OMe2SiO2/2 and MeSi(OH)O2/2, respectively,49,50 Oxygen gas permeability measurements of the coating obtained from the OMCTS/helium APGD were comparable to the untreated polyethylene substrate; see Table 2. In contrast, OMCTS films deposited in a helium/oxygen mixture gave rise to a marked improvement in the gas barrier characteristics of the substrate.

(b) Tetramethylcyclotetrasiloxane Deposition. XPS analysis showed that the hydrophobic TMCTS films deposited in helium contained more oxygen than predicted from the monomer structure; see Table 1. The Si(2p) binding energy was also higher than expected, exhibiting a value (~102.8 eV) akin to a cross-linked structure such as a silsesquioxane21 (Si(2p) binding energy ~103 eV); see Figure 5. Addition of oxygen to the plasma resulted in a diminishment of the Si–H band at ~2200 cm−1.44,52,53 These features can be attributed to Si–O–Si cross-linking with a corresponding partial loss of Si–H functionality. Addition of oxygen to the APGD plasma appeared to augment these phenomena; films deposited in a He/O2 mixture possessed a larger, broader Si–O–Si stretch, a weaker Si–Me band (1260 cm−1), and an almost extinct Si–H peak. A broad band at 3500–3000 cm−1 also emerged, indicative of SiOH–H2O/absorbed H2O2, the presence of which explains the enhanced hydrophilicity of this system.

29Si solid state NMR analysis of the material deposited in helium showed predominantly MeHSiO2/2 at ~30 to ~−40 ppm, a functionality associated with poly(methylhydrogensiloxane) polymer and some entrapped TMCTS; see Figure 7. Bands observed at ~−60 to −70 ppm and ~−80 to ~−90 ppm were indicative of MeSiO3/2 and HSiO3/2, respectively.49,50 Their intensities demonstrated that a significant degree of cross-linking or branching had taken place.

TMCTS coatings deposited from helium APGD did not significantly alter the oxygen permeability characteristics of the polyethylene substrate; see Table 2. In contrast, TMCTS films deposited from a helium/oxygen mixture

---

**Table 2. Oxygen Permeation Measurements**

<table>
<thead>
<tr>
<th>Deposition Conditions</th>
<th>Barrier Improvement Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene substrate</td>
<td>1.0 (by definition)</td>
</tr>
<tr>
<td>OMCTS, 100% He</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>OMCTS, 99% He, 1% O2</td>
<td>6.8 ± 3.5</td>
</tr>
<tr>
<td>TMCTS, 100% He</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>TMCTS, 99% He, 1% O2</td>
<td>4.5 ± 1.6</td>
</tr>
</tbody>
</table>

---

produced a significant improvement in the gas barrier characteristics of the substrate.

**Discussion**

Siloxane coatings deposited from OMCTS in a helium APGD display many XPS and IR spectral features associated with the OMCTS monomer. The observed differences are attributable to the opening and polymerization of the siloxane ring. The high organic content measured and fairly low level of cross-linking (shown by the low Si(2p) binding energy characteristic of linear siloxanes) accounts for the negligible improvement in gas barrier.

The introduction of oxygen into both the OMCTS and TMCTS helium APGD mixtures leads to significant levels of oxygen incorporation at the expense of carbon and hydrogen removal to yield inorganic SiOx cross-linked structures. The accompanying attenuation in oxygen permeation is most likely to stem from a rise in film density (i.e., drop in free volume) and hindrance in segmental mobility associated with an oxidized siliceous phase. A similar fall in oxygen transmission rate has previously been observed for SiOx films deposited by CVD and low pressure PECVD.

**Conclusions**

Introduction of substituted cyclotetrasiloxane precursors into a helium atmospheric pressure glow discharge using an ultrasonic atomizer gives rise to the fast deposition of hydrophobic polysiloxane films onto polyethylene. In the presence of a helium/oxygen gas mixture, SiOx-rich coatings are produced which display a significant improvement in hydrophilicity and gas barrier. This novel combination of a liquid atomizer combined with an atmospheric pressure plasma effectively circumvents a lot of the drawbacks associated with speed and efficiency for conventional vacuum plasma methods.

**Acknowledgment.** L.J.W. thanks EPSRC and Dow Corning for financial support. The authors thank Simeon Bones for his assistance in acquiring solid state NMR spectra, and Dan Futter for useful discussions throughout this work.

LA0204287

---