PLASMA-POLYMERIZED THIN FILMS OF HEXAMETHYLDISILOXANE
PREPARED AT LOW RF POWER

R. Balkova, R. Prikryl, V. Cech, and O. Salyk

Institute of Materials Chemistry, Brno University of Technology
Purkynova 118, CZ-612 00 Brno, Czech Republic

Abstract

We have developed the inductively coupled system for deposition of thin plasma polymer films on solid substrates in RF discharge. The thin films were prepared from vapor of hexamethyldisiloxane (HMDSO) at low RF power to reduce the aging effect in deposited films. The monomer has a relatively simple chemical structure to study the influence of deposition conditions on film properties. The plasma-polymerized (pp) films exhibited an excellent adhesion to the glass substrate. The strong and hydrolytically stable bond could be employed in fibre-reinforced polymer composites if the pp-HMDSO film would be used for surface modification of glass fibers. The pp-HMDSO films were characterized by many techniques suitable to investigate their mechanical and thermal properties, and to determine chemical composition, structure and surface morphology.

1. Introduction

Thin Si-based plasma polymer films (pp-films) are interesting materials for their electronic, optical, mechanical and thermal properties. Especially plasma-polymerized siloxanes as a kind of organosilicon polymers may be chemical and thermal stable materials [1,2]. The HMDSO has a relatively simple chemical structure and it is available for polymerization in rf glow discharge to prepare thin films on glass and silicon substrates. Such a thin layer with good adhesion between the glass substrate and the pp-film may be used as an interlayer between the glass fiber and the polymer matrix in fibre-reinforced composite [3]. But in this case thermally stable films with the hydrolytically stable fibre/matrix bonding are required.

![Figure 1: Schematic representation of the deposition chamber and substrates position.](image-url)
Experiment

The inductive coupling system consists of the reaction chamber made of Pyrex glass with monomer inlet, the vacuum system and the RF generator 40 MHz (Figure 1). Plasma maintaining was standard as described below [4]. A glass plate (39 x 400 x 2 mm$^3$) with substrates was positioned in the reaction chamber and the system was evacuated to 0.5 Pa using rotary and diffusion pumps. To eliminate water from inside surfaces we used an argon flow rate of 10 scem for 1 hour and then we applied argon plasma to clean surface of substrates. The system was again evacuated to 1 Pa and then the monomer vapor, stored in a reservoir, was injected into the reactor chamber at a given flow rate adjusted by a valve to reach the steady-state value of pressure - 10 Pa. The flow rate of the monomer vapor was maintained with respect to the above required pressure. The RF power was turned on and glow discharge polymerization was initiated. Temperature of substrates was not controlled during deposition but after deposition the temperature was about 60 – 70 °C with respect to RF power. When the glow discharge was turn off the argon gas flow (30 scem) was used to cool down the deposited layers.

The thin films were deposited on silicon wafers, glass slides and PET foils at different deposition conditions, such as RF power (< 40 W), time of deposition and flow rate. We have studied distributions of the deposition rate along the chamber axis as a function of RF power (Figure 2) [4].

![Graph showing distribution of deposition rate along the reactor](image)

*Figure 2: Distribution of deposition rate along the reactor*

Plasma process was monitored using the in-situ mass spectrometry. Fragments of the monomer molecules (Table 1) and their partial pressures were studied as a function of time and the RF power. The great reduction of fragments above 20W is evident from Figure 3. We measured time-evolution of monomer fragments after starting plasma deposition as well. We determined that deposition conditions are stabilized after 20 s. It is very important for preparation of thin homogeneous layers.
Table 1: Assignments of HMDSO fragments.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragment</th>
<th>Intensity (a.u.)</th>
<th>Power [W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>H₂⁺</td>
<td>45</td>
<td>OFF</td>
</tr>
<tr>
<td>15</td>
<td>CH₃⁺</td>
<td>59</td>
<td>70</td>
</tr>
<tr>
<td>43</td>
<td>(CH₃)₂Si⁺</td>
<td>66</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>(CH₃)₂SiH₂⁺/ SiOH⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH₃)₂Si⁺/ (CH₃)₂SiO⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH₃)₂Si⁺/ (CH₃)₂SiH⁻</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3: Fragments of monomer molecules and their partial pressures

AFM together with SEM were used to observe the surface morphology and to evaluate the roughness of prepared films. The surface profiles of two different films are plotted in Figure 4. We measured the sample (A), which was situated at the center of plasma discharge. The thickness of the film was 4 μm and the roughness was 20 nm. The second sample (B) with the thickness of 320 nm and roughness of 1 nm was placed 130 nm from the center of discharge.

Figure 4: AFM images of two samples: A was placed under plasma, B was positioned 150 mm from the center of generator coil
FTIR and XPS techniques were used to study chemical composition, structure, and aging effects of thin pp-HMDSO films. We used a Nicolet Impact 400 Fourier transform infrared (FTIR). An absorption subtraction technique was applied to remove the spectral features of Si wafers. These spectra of samples from different positions in the chamber are very similar and show the same chemical structure (Figure 5). We observed aging of all samples by FTIR analysis as well, but the results are without significant changes.

![FTIR spectra of plasma-polymerized film A and HMDSO monomer.](image)

**Figure 5:** FTIR spectra of plasma-polymerized film A and HMDSO monomer.

The dependence of atomic concentrations on the distance \( d \) between sample and the center of plasma discharge is shown in Figure 6. Thin films exhibited aging effect, which was evaluated by comparing the ratios (O/Si and C/Si) of atomic concentrations. Figure 6 demonstrates increase of oxygen concentration and small increase of carbon concentration in the surface layer.

![Atomic composition and ratios of C Si, O Si measured as prepared and after 9 months.](image)

**Figure 6:** Atomic composition and ratios of C Si, O Si measured as prepared and after 9 months.
Thin plasma polymer films were gradually sputtered by Ar ions with the aim to find out concentration depth profile. Determined atomic concentrations across the whole film thickness \( L \) (A - 4600 nm and B - 100 nm) were processed into profiles of element ratios (Figure 7).

Figure 7: Depth profiles of element ratios across the plasma polymer.

A qualitative indication of the adhesion of the thin pp-HMDSO films deposited on Si-wafers at different deposition conditions has been tested using boiling distilled water for 8 hours. After this time the samples were taken out and the adhesion was observed to be excellent. A widely used method of evaluating the adhesion of films is scratch test. Therefore, we have developed a scratch-tester in our institute. A scratch in pp-film formed by the diamond tip together with typical scratch recording of load profile is depicted in Figure 8.

Figure 8: Scratch in plasma polymer film together with scratch recording of load profile.
Adhesion was also appreciated during testing of the lap-shear strength ($\tau$) [5] using the sandwich structures such: A) glass/PES/glass, B) glass /PES/ pp-HMDSO/glass. $\tau_A$ were established as $(3.4 \pm 0.4)$ MPa and $\tau_B$ as $(1.3 \pm 0.4)$ MPa. The reason is bad wettability of pp-HMDSO films by PES resin. There was no observed shift in $\tau_B$ values and therefore it was not possible to determinate the dependence of $\tau_B$ on the deposition conditions. All tensile tests were performed on Universal Testing Machine ZWICK Z010.

The surface free energy [6,7], its dispersive and polar parts, of pp-HMDSO layers deposited on glass slides was estimated on a basis of contact angles measurements against distilled water, ethylenglykol, glycerol and methyleniodide.

<table>
<thead>
<tr>
<th>Power [W]</th>
<th>Contact angle [°]</th>
<th>Surface free energy [mJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glycerol</td>
<td>Methyleniodide</td>
</tr>
<tr>
<td>7</td>
<td>95.4</td>
<td>65.7</td>
</tr>
<tr>
<td>10</td>
<td>90.3</td>
<td>61.1</td>
</tr>
<tr>
<td>30</td>
<td>91.7</td>
<td>62.1</td>
</tr>
<tr>
<td>40</td>
<td>92.1</td>
<td>62.2</td>
</tr>
</tbody>
</table>

*Table 2: Contact angle and surface free energy estimated according to Wu and OWRK (Owends-Wendt-Refel-Kaelbe) methods*

The modulus of layers was estimated using the tensile test of the two-layer composite system that consist of plasma polymer film (pp-HMDSO) and thin substrate (8 µm thick PET foil). $E_{PET}$ changes with temperature and that is why the foil was exposed under the deposition conditions. The pp-film modulus was found to be $(1.0 \pm 0.2)$ GPa (Figure 9).

*Figure 9: Young modulus versus position of the sample in the deposition chamber.*

Conclusion

We developed an inductively coupled deposition system for the preparation of thin films using glow discharge polymerization. The pp-HMDSO films deposited on glass and silicon wafers were characterized by many techniques suitable to investigate their mechanical and thermal properties and determine chemical structure and morphology. Adhesion between film and glass substrate, hydrolytic and thermal stability indicate that these layers could be applied for surface modification of glass fibres intended for fibre-reinforced composites if the wettability would be improved.
Acknowledgment: This work was supported by the contracts GACR 104 00 0708 and COST 527.110.

References