Plasma treatment of organic films: a detailed study of functionalization and degradation using self assembled n-alkylsiloxane Monolayers

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Abstract

The self-assembly of films of the octadecyl derivative (termed OTS) onto the surface of oxidized silicon substrates (SiO\textsubscript{2}/Si), served as model systems for the study of the degradation and functionalization effect of a low pressure low frequency NH\textsubscript{3} plasma. Treatment times in the range of 0.115 s – 1 s was used for this study, since longer treatment times gave rise to a decomposition of the SAM layer due to the ion bombardment in our low frequency discharge. Contact angle and X-ray photoelectron spectroscopy (XPS) measurements were performed on treated samples to investigate the surface modifications created by the plasma. Structural features of the films were also characterized by ellipsometry.

1. Introduction

Plasma treatment of organic substrates leads to the following effects: (i) surface cleaning and etching, (ii) surface functionalization with the introduction of polar groups such as hydroxyl (-OH), carboxyl group (-COOH), carbonyl (-CO) or amino groups (NH\textsubscript{2}), and (iii) crosslinking which is predominant when using a noble gas plasma (e.g. He or Ar). Each of those effects is always present to some degree. However, a polymer often contain additives or contaminant such as oligomers, anti-oxidants, solvents, anti-block agents... which can diffuse to the surface after the plasma treatment and cover the plasma modified surface. The self-assembly of monolayers (SAMs) of the octadecyl derivative (termed OTS for formation from octadecyltrichlorosilane) onto oxidized, planar silicon substrates (SiO\textsubscript{2}/Si) will be a good model for studying the functionalization and the ablation effect of the plasma. In the past, SAMs systems have served as model systems for the study of the interaction of metals deposited on organic films [1-3]. W. E. S. Hunger et al [4, 5] used OTS Self-assembled layers as a model for the assessment of an oxygen plasma effect on polyolefins. Indeed, CH\textsubscript{3}-terminated SAMs are ideal because they represent a truly clean
surface that contains no additives, and their characteristics include: (i) a low density of pinholes in the film, (ii) a uniform film thickness (= 2 nm), (iii) a uniform average of packed aliphatic chains. Ablation is important for the cleaning of contaminated surfaces, for removal of weak boundary layers eventually formed during the fabrication of the polymer. However, this process should be well controlled in order to avoid a degradation of the mechanical properties of the treated polymer, which is possible with the use of SAMs. With regard to the coupling with biomolecules, OH, COOH and NH₂ groups are of special interest. Amino groups with their associated polarity and reactivity can be convenient for the preparation of blood compatible materials [6, 7], or promotion of adhesion for a directed controlled covalent attachment of antibodies in a solid support. Successful plasma induced primary amine incorporations have been reported and discussed earlier [8, 9]. In a previous paper, it has been observed that the kinetics of nitrogen incorporation of ammonia treated surfaces was higher than those treated with nitrogen plasma [10, 11]. Nevertheless, plasma surface functionalization has shown to be not always selective and different chemical groups can also be detected. Indeed, in nitrogen containing plasma gases, the plasma polymer interaction creates not only amine groups, but also imine, amide or cyan groups. Some authors have shown that N₂ plasma treatment leads to bonded nitrogen primarily in the form of imine or imide groups, whereas amine groups are in the majority following NH₃ plasma treatment [12]. Therefore, in this paper, the ability of NH₃ plasma to incorporate amine groups at the polymer surfaces will be discussed. Different complementary surface diagnostic techniques chemical such as contact angle and X-ray photoelectron spectroscopy (XPS) measurements were used on treated polymers to investigate the surface modifications created by the plasma.

2. Experimental: Plasma treatment of polymer substrates

The bell jar-type reactor with an asymmetrical configuration of electrodes consisting of a hollow electrode-grounded cylinder used for the surface has been described elsewhere [11]. The hollow electrode is made of stainless steel and the polymer (22 x 22 cm²) to be treated was rolled onto the grounded cylinder. Commercially available UHP gases were used without further purification (purity of NH₃ is ≈ 99.96 %; N₂ = 99.9 %) and were introduced through MKS mass flow controllers and the pressure was monitored with an MKS capacitive gauge. The main chamber was evacuated by a TPH 170 (Balzers) turbomolecular pumping system and a base pressure of 10⁻³ Pa was obtained. The operating pressure was maintained at 150 - 200 Pa by a 2012 AC chemical pump. The electrical characteristics of the discharge were measured with a Lecroy 9400 digital oscilloscope with a sampling frequency of 100 MHz. Plasma emission was controlled by an optical fiber inserted into the plasma. The radiation transmitted was then focused by means of a quartz lens on the plane slit of a 1 m Jobin Yvon HR monochromator and equipped with a 3600 grooves/mm holographic grating and a Hamamatsu photomultiplier for the analysis of the 300 nm - 450 nm spectral domain.

3. Results and discussion

a) Study of the nitration effect of the plasma

Contact angle measurements (sessile drop) were performed in our laboratory with the help of an image processing system [13]. The reported values correspond to the average of five measurements of the advancing contact angle, performed on different parts of the sample. Typical shifts of ± 3° with respect to the average value were observed. The measurements showed that the ammonia plasma treatment produced highly modified surfaces since the contact angle decreased substantially with the treatment time (figure 1).
Figure 1. Evolution of the water contact angle as a function of treatment time.
(P = 100 Pa; Pw = 5 W; f = 70 kHz)

X-ray photoelectron spectroscopy measurements (XPS) was used to determine the type of polar functionality incorporated on the NH₃ plasma treated SAMs samples. The results showed a time-dependence of the surface concentration of nitrogen, which ranged from 0.5 % in the case of a 0.023 s treatment, to 6-7 % for a 1 s treatment (Figure 2).

Figure 2. Variation of the N1s / C1s peak area ratios as a function of treatment time, for a NH₃ plasma treated C18 SAM. Experimental conditions: Pressure = 100 Pa; Power = 5 W, f = 70 kHz.

The line shape analysis of the N1s spectrum for a treated SAM indicates the presence of highly functionalized groups, even with short exposure times (less than 0.25 s)(figure 3a). The N1s peaks were fitted to four components corresponding to nitrogen in –C≡N (Binding Energy, BE, 398.8 eV), R-NH₂ (BE, 399.9 eV), R-CNH₂ (BE, 401.1 eV). The last peak at 402.2 ev could be ascribed to NO, or to an impurity due to the reaction of amine with ambient CO₂ to produce a carbamate (NHCOOH), as suggested by A. Hooper et al. [14]. With increasing plasma treatment time, the contribution of amine groups becomes predominant (Table 1). It is noteworthy that no amid groups were detected for treatment times higher than 0.5 s, which is surprising since oxygen is present as traces in the reactor (P O₂ = 1%). The position of the amine contribution has been precisely determined by the use of a reducing agent. Indeed, when the reduction with aqueous LiAlH₄ has been performed, the different peaks disappeared excepted the peak at 399.9 ± 0.2 eV, which could be attributed to amine
groups (figure 3b). The strong contribution of amine groups could be attributed to the presence of NH biradicals and H atoms in the discharge, as revealed by optical emission spectroscopy [15].

<table>
<thead>
<tr>
<th>Treatment time (s)</th>
<th>C=NH (398.8 eV)</th>
<th>C-NH₂ (399.9 eV)</th>
<th>CONH₂ (401.1 eV)</th>
<th>N=O or NHOOC (402 eV)</th>
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<tr>
<td>0.02</td>
<td>29</td>
<td>41</td>
<td>21</td>
<td>9</td>
</tr>
<tr>
<td>0.11</td>
<td>25</td>
<td>38</td>
<td>28</td>
<td>9</td>
</tr>
<tr>
<td>0.23</td>
<td>10</td>
<td>47</td>
<td>29</td>
<td>14</td>
</tr>
<tr>
<td>0.5</td>
<td>27</td>
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<td>-</td>
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<td>0.75</td>
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<tr>
<td>1</td>
<td>19</td>
<td>81</td>
<td>-</td>
<td>-</td>
</tr>
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</table>

Table 1: Percentage contribution of functional groups to the total N₁s spectrum as a function of treatment time, for a NH₃ plasma treated C18 SAM. (P = 100 Pa; Power = 5 W, frequency = 70 kHz)
Figure 3: N1s spectrum of a NH3 plasma treated C18 SAM at 5W for 0.11 s; (a) before the reduction and (b) reduced with LiAlH4.

The C1s photoelectron peak for the nontreated C18 SAM consists of a symmetrical peak centered at 285 eV. The surface is quite pure and contains almost no oxygen. The ammonia treatment produced a broadening of the C1s photoelectron peak for very short treatment times (t = 0.11 s). Four carbon peaks were observed at 284.85 eV, 286.1 eV, 287.1 eV and 288.7 eV. The peak at 284.85 eV corresponds to the methyl chain of the SAM. The peak at 286.1 eV could be ascribed to C-N (amine) and/or C-O (alcohol, ether) functions and whereas the peak at 287.1 eV could be attributed to imine (C=N) or carbonyl (C=O) groups. The peak at 288.7 eV could correspond to carboxylic (COOH) or amide groups (CONH2).

b) Surface degradation effect of the plasma

It is well known that low pressure plasmas can create major effects on organic substrates; surface cleaning (ablation), crosslinking and surface chemistry modifications. These effects occur concurrently and depend on processing conditions. In all cases, the plasma is known to affect the topmost surface layer without changing the appearance or bulk properties of the material. Indeed, CH3-terminated SAMs deposited onto oxidized (~ 2 nm) planar silicon substrates (SiO2/Si) can be suitable to estimate the degradation effect of the plasma. The surface morphology of the samples was unaffected by the treatment, within the resolution of Scanning electron microscopy (SEM) observations. With the short plasma treatment times used, it seems that the etching effect is likely to be on a nanometric scale. We have thus used ellipsometry measurements. The plasma treatments of SAMs samples gave rise to bond scissions which were confirmed by ellipsometry measurements showing that molecular layers were removed from the substrate (Table 2). For long treatment times (t > 1 s), a complete loss of the C18 SAM was observed, since the difference of the thickness before and after the plasma treatment (Δe) was close to 2 nm, corresponding to the total thickness of the OTS film. Surface analysis by XPS showed that the N/C ratio increased sharply at first (t < 0.11 s) and a plateau was obtained with a value around 6-7 % after 0.5 s of treatment time. It has been shown that a nitrogen uptake of 2-3 % was enough to assure a density of one NH2 function/alkyl chain. The optimum treatment time therefore should be chosen in such a way as to have a maximum of nitrogen grafted onto the surface, with a minimum ablation effect. This optimum treatment time according to table 2 is around 0.1 s.

<table>
<thead>
<tr>
<th>Treatment time (s)</th>
<th>Δe (nm)</th>
<th>N1s/C1s (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non treated</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
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<tr>
<td>1</td>
<td>1.7</td>
<td>6</td>
</tr>
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</table>

Table 2. Ellipsometry and N/C atomic ratio measurements, as function of the NH3 Plasma treated C18 SAM
Conclusion:

A bell jar-type reactor with an asymmetrical configuration of electrodes has been used for the surface modification of self-assembled monolayers (SAMs). Treatment times in the range of 0.115 s – 1 s was used for this study, since longer treatment times gave rise to a decomposition of the SAM layer due to the ion bombardment in our low frequency discharge [16]. Contact angle measurements on NH3 plasma treated SAMs displayed an increase of the wettability when the treatment time was increased, revealing the incorporation of polar functions. XPS spectra showed a time-dependence of the surface concentration of nitrogen. Structural features of the films, characterized by ellipsometry showed an optimum treatment time (t > 0.5 s) above which OTS films started to degrade, showing in this way the role of the energetic ions in the denitrogenation process.

References