The effect of surface reactions of O, O₃ and N on film properties during the growth of silica-like films

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The effect of surface reactions of O, O₃ and N on film properties during the growth of silica-like films

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Abstract
The effect of surface reactions of O, O₃ and N radicals during the growth of silica-like (SiOₓCᵧHₚ) films on film properties is investigated. A SiOₓCᵧHₚ film is deposited from a He/Hexamethyldisiloxan (HMDSO) cold atmospheric plasma on a rotating substrate. The surface of this film is, during the growth, treated on the opposite side of the substrate by a second cold atmospheric plasma with helium and an addition of O₂ or N₂. A reactor with four separated cells and gas curtains between them is used to avoid cross-contamination of the ambient atmosphere in each cell. The changes in film composition after the deposition with and without a treatment by O, O₃ and N are investigated by Fourier transform infrared spectroscopy and x-ray photoelectron spectroscopy. Additionally, the effect of each species on the deposition rate is also presented and discussed.

Keywords: silicon dioxide, FTIR, atmospheric pressure plasma, microplasma, deposition

1. Introduction
Knowledge of plasma–surface interaction mechanisms is very important for the understanding and optimization of plasma deposition processes. However, the analysis of any plasma based deposition mechanism is a very complex process, because fluxes of many reactive species, ions with high kinetic energy, photons or energetically excited particles, are combined at the same time and result in a complex surface chemistry. A combination of several diagnostic techniques is almost always necessary. A more detailed understanding of the role of single particles in the deposition process can be achieved in beam experiments, where the plasma process is simulated by a combination of several quantitatively calibrated sources [1] in an ultra-high vacuum chamber.

This approach is, however, difficult to apply to the study of the deposition processes from plasmas generated at atmospheric pressure. These plasmas offer the possibility to deposit on vacuum incompatible materials and are, therefore, of interest to the industry. They can also be relatively easily integrated into production lines. However, the high collision frequency results in complex chemistry, filamentation and localization of the plasma and absence of ion bombardment. These factors limit the number of material systems that can be deposited, and they also make plasma diagnostics very difficult. One possible way to overcome some of the disadvantages is the use of cold atmospheric microplasma jets, where a homogeneous plasma can be generated in a small volume and can be used for a localized deposition or surface treatment. This was demonstrated successfully in the example of SiO₂-films [2–5]. The localized treatment can be a disadvantage for large area deposition application, but we will demonstrate in this article that this localization of the treatment can be used effectively to study the surface reaction of different reactive species. Reactions can be isolated from each other in a similar way to that performed in beam experiments, but under conditions very similar to deposition conditions.

Silicon dioxide is a widely used material in the semiconductor industry. It is used as a scratch resistant layer, as a protective layer against corrosion, or as a diffusion barrier on polymer surfaces. Organosilicon molecules, especially hexamethyldisiloxane (HMDSO), are the common precursors because of their non-toxicity, ease of use, and lower tendency of dust formation. Deposition of SiO₂ from HMDSO on foils, steel, wood or textile has been reported in the past [6–9]. The plasma sources for large area deposition are...
usually different modifications of dielectric barrier discharges (DBDs), where the treated surface is placed on one electrode and serves also as a dielectric barrier [10–12]. However, a glow mode or Townsend mode of the DBD without formation of localized streamers is a necessary condition for obtaining homogeneously thin films [12]. As already mentioned, an alternative to these deposition sources are the atmospheric pressure microplasma jets, which can be used for a local deposition of silica-like films or, as will be discussed here, for a study of fundamental surface reaction mechanisms involved in atmospheric pressure plasmas in general.

Typically, deposition without the addition of an oxidizing particle (e.g. O₂ or N₂O) leads to carbon rich SiOₓCᵧHᵣ films. Only after the addition of oxygen-containing species does this result in the structural change to SiO₂-like films. We have shown recently [13] that the carbon is removed mainly in surface reactions of atomic oxygen, and several tests on the penetration depth and the amount of oxygen needed to remove the carbon have been made [14]. Furthermore, the treatment of SiOₓCᵧHᵣ with other species has been investigated. The treatment of SiOₓCᵧHᵣ films with a coaxial jet operating with argon has revealed that Ar ions and/or Ar excited species (e.g. metastables) can also reduce the carbon content in these films [14]. The concept of alternative deposition and treatment has been transferred to a DBD operating with nitrogen. Again, a reduction of the carbon content has been observed [15].

In this study, we investigate the surface reactions and resulting effects of additional species (O₂ and N₂) and compare them to effects induced by O atoms. Moreover, a new reactor concept with four separated cells and independently controlled atmospheres, which are facing the same rotating substrate, with in situ Fourier transform infrared spectroscopy (FTIR) diagnostics is introduced.

2. Experimental setup

The plasma source used in this study is a radio frequency driven parallel electrode microscale atmospheric pressure plasma jet (µ-APPJ). The setup is shown in figure 1. A detailed description can be found elsewhere [13, 14].

The µ-APPJ consists of two parallel electrodes. The electrodes have a thickness of 1 mm and are either 10 or 30 mm long. The distance between them is 1 mm. The electrodes are fixed by two glass plates forming the discharge channel. One electrode is grounded, the other one is driven with a frequency of 13.56 MHz and a root-mean-square voltage of either 230 V (O₂) or 210 V (N₂). Helium is used as the working and plasma forming gas at either 5000 sccm (standard cubic centimetre per minute) for He/HMDSO plasma or 1400 sccm for He/O₂ or He/N₂ plasmas. For the deposition of SiOₓCᵧHᵣ films HMDSO was admixed. For the treatment, O₂ or N₂ was admixed.

The reactor setup, shown in figure 2, has four special features to provide better control over the deposition process:

(i) rotating substrate for sequential deposition/treatment
(ii) four separated cells for multi-source application
(iii) gas curtains for cell separation
(iv) in situ film diagnostic.

The four cells can be used to install four independent microplasma sources or be used for in situ diagnostics. The rotating substrate provides the flexibility to deposit and/or treat the same sample with the different microplasma sources sequentially. The deposition/treatment trace has a diameter of 80 mm. To avoid the diffusion of gas from one cell/jet to another, a gas curtain has been established. The concept is shown in figure 3. The four cells are integrated in a reactor block and all face a 100 mm diameter silicon wafer placed on a rotating substrate. The gap between the reactor block and the wafer is less than 0.5 mm to minimize the gas conduction among the cells. Additionally, two long and deep gaps with gas in and gas out connections are manufactured between the cells as shown at figure 3. Through one slot Ar is fed into the cell and gas is pumped out through the other one, so that the gas flows against the rotation direction of the substrate. This gas flow prevents the diffusion of gas between the cells. Ar is used as a separation gas at a total flow rate of 15 slm (standard liter per minute) through these four slots. The effectiveness of the gas separation is described in detail below (section 2.1). An additional pumping slot is on the reactor axis. For the
in situ diagnostics a FTIR setup has been installed. With the help of several mirrors the infrared beam is directed into the chamber and focused on the sample through a circular aperture of approximately 2 mm. For the deposition process the chamber is filled with the working gas and the pressure is kept at one atmosphere by pumping.

2.1. Cell separation

The quality of the cell separation is evaluated by two central questions. First, how much of the separation gas diffuses into each cell? And second, how much gas diffuses from one cell to the other and contaminates its atmosphere? To maintain experimental conditions Ar was used as a separation gas at a flow rate of 15 slm through the four slots. The frequency of the rotating substrate was set to 5 Hz. The detection of gas contamination from the separation and from another cell was determined by optical emission spectroscopy, where helium test plasma was used to excite the gas in the cell. The electrodes were, therefore, directly facing the adjacent atmosphere in the corresponding cell, and there has been no forced He flow directly between the electrodes. 5000 sccm of He gas has been injected at the side of the cell. To study the penetration of the curtain gas (in this case argon) into the cell, the emission intensity of the 750.52 nm Ar-line from the test plasma was recorded during the operation and compared to its intensity at the He/Ar gas mixture with known Ar concentration (signal calibration). The intensity of the Ar emission line during the substrate rotation corresponded to an admixture of 1% of Ar in He. In other words, only 50 sccm of Ar reach the atmosphere of the cell with an He gas flow of 5000 sccm. This contamination decreases strongly at lower rotation frequencies.

The diffusion of gas between different cells has been quantified with the same approach. In addition to He flow in one selected cell and argon curtain flow, the opposite cell has been filled by nitrogen gas with a flow of 3000 sccm. Again, the test plasma has been turned on in the cell filled by He and the nitrogen emission feature at 336 nm has been followed and calibrated again by using Ar/N2 with a known N2 concentration as a curtain gas. The intensity of the emission line of nitrogen detected in the helium plasma corresponds to an admixture of less than 2% of N2 into Ar. Since only 50 sccm of the separation gas enters the He plasma cell, the nitrogen flow into the tested cell is only 1 sccm. So only 0.02% of N2 from the second cell reaches the tested plasma cell. Taking into account that the usual admixtures of N2, O2 or HMDSO to a main flow of He or Ar is less than 1%, the level of contamination in the opposite cell is less than 2 ppm. This is below the impurity level in He and Ar gases used and confirms the effectiveness of the cell separation.

2.2. Experimental parameters

In this article, the deposition process will always be the same. Only the parameters for the treatment plasma are changed. The experimental conditions are summarized in Table 1. In one cell a SiOxCyHz film is deposited, in the opposite cell this film is treated with either a He/O2 or an He/N2 plasma. The substrate is rotating with a frequency of 5 Hz.

The deposition is carried out with the APPJ with an electrode length of 10 mm. The He flow rate is 5000 sccm. The HMDSO is vaporized in a bubbler system. The He flow of 8 sccm corresponds to an HMDSO flow of 0.1 sccm. To obtain a constant flow rate the HMDSO was kept at 0 °C. The applied voltage was 230 V. These conditions have been used in our previous works [13, 14].

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The oxygen plasma treatment is carried out with the APPJ with an electrode length of 10 mm. The He flow rate is 1400 sccm and the oxygen admixture is 0.6%. The applied voltage is 230 V. In this particular case the Ar cell separation is not used and the pumping is done through all of the slots.

The nitrogen plasma treatment was carried out with the APPJ with an electrode length of 30 mm. The He flow rate was 1400 sccm and the nitrogen admixture was 0.3%.

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**Table 1. Overview over the deposition and different treatment conditions.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Deposition</th>
<th>Oxygen treatment</th>
<th>Nitrogen treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma source</td>
<td>APPJ</td>
<td>APPJ</td>
<td>APPJ</td>
</tr>
<tr>
<td>Electrode length</td>
<td>10 mm</td>
<td>10 mm</td>
<td>30 mm</td>
</tr>
<tr>
<td>Gas mixture</td>
<td>5000 sccm He</td>
<td>1400 sccm He</td>
<td>1400 sccm He</td>
</tr>
<tr>
<td></td>
<td>20 ppm</td>
<td>0.6 % O2</td>
<td>0.3 % N2</td>
</tr>
<tr>
<td>HMDSO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate distance</td>
<td>4 mm</td>
<td>4–30 mm</td>
<td>4 mm</td>
</tr>
<tr>
<td>Voltage</td>
<td>230 V</td>
<td>230 V</td>
<td>210 V</td>
</tr>
</tbody>
</table>

---
FTIR (Bruker, IFS66/S) in transmission is used to analyse chemical bonds in the films. The resolution of the spectra used is 4 cm\(^{-1}\). SiO\(_2\) has three characteristic absorption peaks due to rocking, bending and asymmetrical stretching. The asymmetrical stretching absorption is the most intense peak, in the region of 1000–1200 cm\(^{-1}\). In carbon-containing films additional peaks can be observed for Si–(CH\(_3\))\(_2\) rocking, Si–O–C asymmetrical stretching, Si–(CH\(_3\))\(_3\) bending and C–H stretching. Additionally, absorption peaks of SiOH can be detected in the films. The position of the main peak shifts to lower wavenumbers. The distance of the oxygen treatment is still visible, but not as effective as for short distances. On moving the treatment jet further away, to 20 and 30 mm, the observed trend in the spectra is smaller than the peak in the reference spectra. An effect of the oxygen treatment is still visible, but not as effective as for short distances. On moving the treatment jet further away, to 20 and 30 mm, the observed trend in the spectra continues. The integrated absorption per \(\mu\)m of the main peak.

### 3. Experimental results

#### 3.1. Treatment with He/O\(_2\) plasma

In a He/O\(_2\) plasma, atomic oxygen and ozone are produced. The atomic oxygen and ozone densities were measured with molecular beam mass spectrometry (MBMS) [23] for the same experimental conditions, but with an electrode length of 30 mm. Since the atomic oxygen density along the plasma channel saturates after less than 10 mm distance [24], the results are representative for our He/O\(_2\) plasma as well. It has been measured that close to the substrate the atomic oxygen density is at its maximum, whereas the ozone density is much lower. Moving away from the substrate, the atomic oxygen density decreases as O recombines with O\(_2\) to O\(_3\), and the ozone density increases (see figure 4). Therefore, a distance variation of a treatment with He/O\(_2\) plasma is carried out to distinguish between the effect of atomic oxygen and ozone on the film structure.

For the reference spectra a film is deposited and treated with a flow of He with only 0.2% oxygen, without plasma being ignited. In figure 5 the FTIR spectra of films obtained for the He/O\(_2\) plasma treatment, with distance varied from 4 to 30 mm, are shown.

The reference spectra shows a carbon-containing film. This is indicated by the absorption peaks around 1260, 800 and 2960 cm\(^{-1}\). For a distance of 4 and 10 mm all these carbon related peaks disappear. The absorption per \(\mu\)m of the main peak is stronger and the peak is shifted to higher wavenumbers. These are indicators for a change from a SiO\(_2\)-like film to a SiO\(_2\)-like film. These changes are different for a distance of 15 mm. In comparison to the treatment at a distance of 10 mm the absorption per \(\mu\)m decreases and the position of the main peak shifts to lower wavenumbers. The carbon related peak around 1260 cm\(^{-1}\) is clearly visible, but is smaller than the peak in the reference spectra. An effect of the oxygen treatment is still visible, but not as effective as for short distances. On moving the treatment jet further away, to 20 and 30 mm, the observed trend in the spectra continues. The integrated absorption per \(\mu\)m of the main peak.

### Table 2. Main absorption features of SiO\(_2\)-C\(_x\)-H\(_y\) films.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–O–Si</td>
<td>450</td>
<td>Rocking</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>Bending</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>1075 (AS1), 1150 (AS2)</td>
<td>Asymmetric stretching</td>
<td>[16]</td>
</tr>
<tr>
<td>Si–(CH(_3))(_2)</td>
<td>800</td>
<td>Rocking</td>
<td>[17]</td>
</tr>
<tr>
<td>Si–(CH(_3))(_3)</td>
<td>840</td>
<td>Rocking</td>
<td>[17]</td>
</tr>
<tr>
<td>Si–O–C</td>
<td>1035, 1100</td>
<td>Asymmetric stretching</td>
<td>[17, 18]</td>
</tr>
<tr>
<td>Si–(CH(_3))(_2)</td>
<td>1270</td>
<td>Bending</td>
<td>[19]</td>
</tr>
<tr>
<td>Si–(CH(_3))(_3)</td>
<td>1260</td>
<td>Bending</td>
<td>[19]</td>
</tr>
<tr>
<td>Si–(CH(_3))(_3)</td>
<td>1250</td>
<td>Bending</td>
<td>[19]</td>
</tr>
<tr>
<td>sp(^3)CH(_3)</td>
<td>2960</td>
<td>Asymmetric stretching</td>
<td>[17]</td>
</tr>
<tr>
<td>OH</td>
<td>930</td>
<td>Bending</td>
<td>[20]</td>
</tr>
<tr>
<td>OH</td>
<td>Around 3350</td>
<td>Stretching of hydrogen bonded Si–OH</td>
<td>[20]</td>
</tr>
<tr>
<td>OH</td>
<td>3650</td>
<td>Stretching of free Si–OH</td>
<td>[20]</td>
</tr>
<tr>
<td>Si–N–O</td>
<td>900–1000</td>
<td>Bending</td>
<td>[21]</td>
</tr>
<tr>
<td>NH</td>
<td>3400</td>
<td>Stretching of Si–NH</td>
<td>[18]</td>
</tr>
</tbody>
</table>
structure between 1000–1200 cm$^{-1}$ becomes smaller than for the untreated sample, but they are located at the same position. The carbon peak around 1260 cm$^{-1}$ is smaller for the long distance treatment than with no treatment. Further changes can be observed in the Si–OH absorption in the region between 3000 and 4000 cm$^{-1}$. In a distance shorter than 15 mm a clear absorption of OH is visible. For larger distances and for the reference spectra no absorption feature, due to OH, can be observed. The OH absorption accords with the changes in the ratio of the main peak around 1070 cm$^{-1}$ to its shoulder around 1150 cm$^{-1}$. Both the OH absorption and the main peak to shoulder ratio can be assigned to a certain porosity in the films [20, 25]. For the SiO$_x$C$_y$H$_z$ films the OH absorption cannot be used as a reference for the porosity [26].

### 3.2. Effect of atomic oxygen

The spectra, at distances of 4 and 10 mm, and their differences to the reference spectra are shown in Figure 6. All carbon related absorption features at $\sim$800, $\sim$850, $\sim$1260 and $\sim$1030 cm$^{-1}$ disappear and peaks at $\sim$1070 cm$^{-1}$ and 1130–1150 cm$^{-1}$, corresponding to new Si–O–Si bonds, appear.

The most obvious is the change in the Si–(CH$_3$)$_3$ bending absorption between 1250 and 1270 cm$^{-1}$, where there is no overlap with other absorption features. The disappearance at $\sim$1265 cm$^{-1}$ indicates a full removal of all methyl groups.

Corresponding to this observation is the change in the absorption due to the rocking of Si–(CH$_3$)$_2$ and Si–(CH$_3$)$_3$ in the regions around 800 cm$^{-1}$ and 840 cm$^{-1}$, respectively. The reduction of both peaks, again, indicates a loss of methyl groups. Since Si–O–Si bending is also located at 800 cm$^{-1}$ the changes are difficult to clearly assign.

Further changes can be seen in the region between 1000 and 1250 cm$^{-1}$. Several peaks for the Si–O–C and Si–O–Si asymmetric stretching absorption can be found in this region. Peaks at $\sim$1030 and $\sim$1100 cm$^{-1}$ (see the discussion to the ozone treatment below) are removed and peaks at $\sim$1070 and $\sim$1130–1150 cm$^{-1}$ appear in this region. The absorption feature in the 1000 to 1250 cm$^{-1}$ region correlates well with just two absorption peaks (Gauss profile) positioned at the $\sim$1070 and $\sim$1130–1150 cm$^{-1}$ wavenumbers. The appearance of these two components is due to the formation of new Si–O–Si bonds. The other missing features are in agreement with complete carbon removal.

Figure 7 shows the direct comparison of the spectra for a treatment at 4 and 10 mm. For the 4 mm treatment the absorption at $\sim$1070 cm$^{-1}$ (AS1) and $\sim$800 cm$^{-1}$ is larger and less OH ($\sim$930 cm$^{-1}$) is incorporated into the films. The shoulder at around 1150 cm$^{-1}$ (AS2) stays constant and, therefore, the AS2/AS1 peak ratio, which scales roughly with film porosity [25, 27], decreases. These changes are a strong indication that with much higher O atom flux a denser and more cross-linked film is produced.

For the treatment at 15 mm distance, methyl groups are also removed, as can be clearly seen in the reduction of the Si–(CH$_3$)$_3$ and Si–(CH$_3$)$_2$ bending, but a peak at 1270 cm$^{-1}$ due to Si–(CH$_3$)$_1$ bending remains. Also the rocking absorption due to Si bonded methyl groups is not completely removed. Changes in the region between 1000 and 1250 cm$^{-1}$ are not as strong as for the short distance treatment. The main peak in the difference spectra is shifted to lower wavenumbers. This is
due to the Si–O–C bonded carbon, whose absorption features are located at lower wavenumbers than those of Si–O–Si, and which are still present in the material after the treatment at the distance of 15 mm. Clearly, the flux of atomic oxygen to the surface is not large enough to remove all carbon from the film.

3.3. Effect of ozone

It has been shown above that ozone is the dominant species at distances from 20 mm onwards and that the oxygen density is much smaller in this region. Therefore, the effect of ozone on the film structure is mainly visible in the films treated at distances of 20 and 30 mm. To analyse the changes, the reference spectra is again subtracted from the spectra of the treated films. Figure 8 shows the obtained difference. The same changes can be seen for both films, corroborating that the effect of atomic oxygen can be neglected and mainly the effect of ozone, whose density varies only slightly at these distances, is observed.

The following changes are observed. Peaks disappear at ∼800, ∼845, ∼1030, ∼1102 and ∼1265 cm\(^{-1}\). No new absorption features appear. Similarly to the 15 mm treatment, the absorption for Si–(CH\(_3\))\(_2\) and Si–(CH\(_3\))\(_3\) bending disappears and only Si–(CH\(_3\))\(_1\) bending absorption at 1270 cm\(^{-1}\) remains. Corresponding to this is the reduction of Si–(CH\(_3\))\(_2\) and Si–(CH\(_3\))\(_3\) rocking absorption in the regions of 800 cm\(^{-1}\) and 840 cm\(^{-1}\) respectively. The Si–(CH\(_3\)) rocking, located at ∼765 cm\(^{-1}\), would be expected to appear but cannot be clearly identified due to noise in the spectrum.

Further changes can be seen in the region between 1000 and 1200 cm\(^{-1}\). Taking into account the observations described above, one can suppose a change in the Si–O–C asymmetric stretching absorption for Si–O–CH\(_3\) and Si–O–CH\(_2\), located at 1100 cm\(^{-1}\). This is consistent with the other changes in the spectra. The change at 1030 cm\(^{-1}\) is due to a small reduction of the Si–O–C stretching component. The larger change at 1100 cm\(^{-1}\) compared to 1030 cm\(^{-1}\) is probably due to the fact that the former peak corresponds to the absorption of Si–O–C bonds located on internal surfaces of small pores. The carbon located at these bonds likely exhibit a larger reaction probability with ozone than with carbon located in the Si–O–C bonds in bulk material.

In summary, modifications by ozone are limited only to a removal of carbon-containing, mainly methyl, groups. Compared to the atomic oxygen treatment, the ozone is not able to generate new Si–O–Si bonds.

Deposition rates of films deposited during the He/O\(_2\) plasma treatment and that of the reference film are shown in figure 9. The deposition rate is enhanced in the same way (∼1/3 faster) for all treatments, except the treatment at 4 mm distance.
where the deposition rate is more than doubled compared to the reference process. Taking into account that the deposition process itself is always the same, the treatment of the surface with ozone or with O atoms changes the surface passivation by methyl groups or hydrogen atoms, which consequently enhances the surface reaction probability of growth precursors in the depositing process. We have discussed before that these growth precursors are very probably O–Si–(CH₃)₃ radicals with a sticking probability of at least 10% [28]. The increase of this surface reaction probability is a plausible explanation of the observed effect. The very high deposition process at the He/O₂ treatment at 4 mm distance is related to the structural changes discussed above. A very high flux of O atoms under these conditions results in larger cross-linking and a denser material. There is a higher likelihood of incorporating more Si atoms into the film resulting in a larger deposition rate.

3.4. Effect of nitrogen

Reuter et al [15] have shown that the treatment of SiOₓCᵧHᵥ films by DBD Townsend discharge in N₂ can also result in carbon free SiOₓ-like films. Therefore, we have tested a treatment with a He/N₂ plasma in a µ-APPJ at a distance of 4 mm and with nitrogen admixture of 0.3%, where the atomic nitrogen density is at its maximum [29]. The preliminary measurements of the N absolute density by means of MBMS estimate this density to be in the range 1.3 × 10¹⁴ cm⁻³ [30], lower than the density of atomic oxygen. As a reference spectra a film was deposited and treated with a flow of helium with 0.3% N₂ only, without plasma being ignited. The same analysis as for the treatment with He/O₂ plasma is carried out here. Figure 10 shows the reference spectra, the film spectra and again the difference, obtained by subtracting the reference spectra from the film spectra.

The following changes are observed after the treatment with N atoms. The removal of Si–(CH₃)₃ and Si–(CH₃)₂ absorption features and the appearance of new Si–(CH₃)₁ groups in the wavenumber region 1240–1285 cm⁻¹ is clearly visible. After the treatment mainly single methyl groups are absorbing in the film. This change can also be seen in the region of 750–840 cm⁻¹, where the absorption due to Si–(CH₃)₁ and Si–(CH₃)₂ rocking at 840 cm⁻¹ and 800 cm⁻¹, respectively, decreases. This change resembles the effect of ozone where, however, no new absorption at ~1275 [Si–(CH₃)₁] has been observed. Furthermore, the absorption due to sp³CH₃ asymmetric stretching at around 2960 cm⁻¹ disappears. Contrary to ozone treatment, an increase in the absorption can be seen in the region between 1000 and 1240 cm⁻¹. Features with a maximum around ~1050 and ~1140 cm⁻¹ appear. Compared to the oxygen treatment at short distances, where the atomic oxygen is dominant, these new features are positioned at lower frequencies. This is probably due to nitrogen incorporation into the film [31]. Additional absorption features are observed at around 3400 and 930 cm⁻¹, which can be related to NH, Si–N–O or also OH absorptions. Surprisingly, the nitrogen treatment does not enhance the deposition rate, it stays the same as measured for the case of reference spectrum.

![Figure 10. Nitrogen treatment: original spectra and difference, obtained by the subtraction of the reference from the spectra. (a) Reference spectra only, (b) spectra of the film and the difference.](https://example.com/figure10)

XPS measurements of the nitrogen-treated sample have confirmed a small incorporation of nitrogen into the film. The stoichiometry is 60% oxygen, 30% silicon, 7% carbon and 3% nitrogen. A further investigation of the chemical bonds was performed. Each element was fitted with two components, the results are summarized in table 3. The major components of the oxygen 1s peak and the silicon 2p peak are positioned at 533.1 eV and 103.6 eV respectively. They can be assigned to SiO₂ [22]. The nitrogen peak positioned at 400.2 eV and the carbon peak at 286.4 eV can be assigned to C=N bonds [34]. The major component of the carbon peak at 284.8 eV refers to C–C or C–H bonds. The second component of the nitrogen peak at 398.9 eV cannot be clearly assigned. C–N bonds are reported to be at 398.46 eV, but no corresponding component at 287.32 eV is visible in the carbon peak [22]. The N–Si bonds in Si₃N₄ are reported at 398.4 eV for the nitrogen peak and at 102.3 eV for the silicon peak [33]. This corresponds very well with our observation, where a component of nitrogen is located at 398.9 eV and a silicon component at 102.7 eV. Some N–H bonds are also located in this region: (Si)₂N–H at 398.0 eV and Si–N(H₂) at 398.6 eV [35]. N–N and N–O bonds are expected to be at 387.8 eV and 404.0 eV respectively [36] and cannot be observed in the XPS spectra. The silicon component at 102.7 eV can be assigned to Si–N bonds, as described above, but also to some suboxide bonds, that are usually in the region between 101.5 to 102.8 eV [37]. Si–H as well as Si–C bonds can be ruled out, since they should be located at 100.8 eV [32], and at 99.3 eV respectively [38]. Si–C bonds can also not be observed in the carbon peak. The absence of Si–C bonds in the XPS does not correspond to the FTIR spectra, where absorption due to Si–(CH₃)₁ bending and rocking can be observed. Since XPS is a surface sensitive method, we assume that Si–C bonds were removed at the surface during the sputter process with Ar⁺ ions and are, therefore, not detectable by XPS.
Table 3. XPS components of O 1s, Si 2p, N 1s and C 1s peak: binding energy (BE), ratio of the bond of the total spectra, ratio of the bond of the single element, corresponding bond and binding energy in the reference.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic percentage</th>
<th>BE (eV)</th>
<th>Ratio total</th>
<th>Ratio element</th>
<th>Bond</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>60 at%</td>
<td>533.1</td>
<td>47.82</td>
<td>80.09</td>
<td>Si–O</td>
<td>533.1 [22]</td>
</tr>
<tr>
<td>Si</td>
<td>30 at%</td>
<td>102.7</td>
<td>5.17</td>
<td>17.35</td>
<td>Si–N</td>
<td>BE(SiO 2)−1.0 [33]</td>
</tr>
<tr>
<td>N</td>
<td>3 at%</td>
<td>398.9</td>
<td>2.32</td>
<td>72.27</td>
<td>Si–N</td>
<td>398.7 [33]</td>
</tr>
<tr>
<td>C</td>
<td>7 at%</td>
<td>284.8</td>
<td>5.13</td>
<td>70.37</td>
<td>C–C/CH</td>
<td>284.64 [34]</td>
</tr>
</tbody>
</table>

The oxygen peak is located at higher binding energies and might be assigned to OH in H 2O [32] as it is also observed in the FTIR spectra.

To conclude the XPS measurements, the film is primarily silicon dioxide with a small nitrogen and carbon content. Nitrogen is mainly bonded to two silicon atoms or hydrogen. Since the amount of nitrogen is small, the assignment of bonds is difficult. However, the XPS results correspond, except for the missing Si–C bond, very well to the described changes in the FTIR spectra.

Additionally we can conclude that the effect of the treatment with the He/N 2 plasma results in different film changes than those observed by Reuter et al [15] for N 2 DBD plasma in Townsend mode, where no carbon, NH, OH or Si–N–O related absorption features were observed in the FTIR spectrum. We assume that in the plasma jet treatment nitrogen atoms are responsible for the changes in the film and that they can be incorporated into it. In the treatment with the DBD, the nitrogen metastable density is 10 4 times higher than the electron density [11]. Thus we assume that, in the case of the treatment in the DBD, the metastables are responsible for the composition changes but they are not incorporated into the film.

3.5. Comparison of all treatments

Figure 11 shows the direct comparison of the spectra resulting from the He/O 2 plasma treatment at 4 mm (oxygen) and 30 mm (ozone), and the treatment with He/N 2 plasma at 4 mm. The following differences are observed: the strongest effect on the film structure is atomic oxygen. It can remove all carbon, result in denser films and accelerate deposition rate significantly. While the effect of nitrogen atoms is smaller than the effect of oxygen atoms, it is stronger than the effect of ozone. The main peak position of nitrogen-treated films is shifted to higher wavenumbers, but not as far as for the oxygen treatment. The higher absorption indicates a more SiO 2-like character with some incorporated nitrogen in the silica network. The bending peak of (CH 3) is also shifted to higher wavenumbers, indicating that only single methyl group is bonded preferentially to silicon atoms. This is consistent with the changes in absorption between 800 and 850 cm −1, as discussed above. These results indicate that neither nitrogen atoms nor ozone are able to remove single methyl groups bonded to silicon atoms.

Figure 11. FTIR spectra from the oxygen treatment at 4 mm (oxygen), at 30 mm (ozone), and the nitrogen treatment.

At 930 cm −1 a very similar, though slightly smaller, absorption can be seen for the nitrogen-treated films as for the atomic oxygen treated films. However, looking at the region of 3000 to 3600 cm −1 where another absorption peak is located, one can observe differences. The difference in the absorption is due to the fact that absorption of Si–N–O and NH groups is also located at these wavenumbers and the peaks in nitrogen-treated films can be composed of OH, Si–N–O and NH absorptions [18]. The large overlap does not, unfortunately, allow the separation of their contributions. Very low OH absorption at 930 cm −1 and 3000–3600 cm −1 is observed for ozone-treated films.

4. Conclusion

The effects of surface reactions of oxygen atoms, ozone and nitrogen atoms on the properties of SiO x C y H z films have been studied in the multi-plasma-cell reactor with rotating substrate. The SiO x C y H z films have been deposited from He/HMDSO plasma on the rotating substrate and treated continuously on the opposite side of the substrate by O dominated conditions (He/O 2 plasma at 4 mm distance), ozone dominated conditions (He/O 2 plasma at 30 mm distance) and N dominated conditions (He/N 2 plasma at 4 mm distance). The reactor with four separated cells and with gas curtains between them has been
used to avoid cross-contamination of the ambient atmosphere of each cell. The resulting FTIR spectra of treated films have been compared to each other and also to corresponding reference spectra.

The following effects have been observed. Ozone causes the smallest changes, which are limited only to the removal of carbon-containing, mainly methyl, groups. Ozone is not able to generate any new Si–O–Si bonds and also no absorption features due to OH groups appear. On the other hand, the ozone treatment increases by 1/3 the deposition rate of the film, probably due to reduced passivation and enhanced surface reactivity of the film surface. Changes in the FTIR spectrum after treatment containing atomic nitrogen are more significant, resulting in an increase and shift of the absorption features in the main absorption structure in the 1000–1250 cm\(^{-1}\) region. However, the increase and the shift is still smaller than in the case of the treatment dominated by atomic oxygen. The methyl groups are removed in a similar way as during the treatment with ozone. Additionally, absorption around 930 cm\(^{-1}\) and from 3000–3600 cm\(^{-1}\) indicates the presence of new OH, NH and also Si–N–O groups. The XPS measurements of the composition shows that the film contains 3% nitrogen, mainly bonded to silicon. Atomic oxygen causes the most significant changes. Besides the removal of all carbon related absorption features, new Si–O–Si bonds appear and OH absorption is visible in the spectrum. For very large O fluxes to the surface, the deposition rate is more than doubled and denser films with the smallest changes, which are limited only to the removal of carbon-containing, mainly methyl, groups. Ozone is not able to generate any new Si–O–Si bonds and also no absorption features due to OH groups appear. On the other hand, the ozone treatment increases by 1/3 the deposition rate of the film, probably due to reduced passivation and enhanced surface reactivity of the film surface. Changes in the FTIR spectrum after treatment containing atomic nitrogen are more significant, resulting in an increase and shift of the absorption features in the main absorption structure in the 1000–1250 cm\(^{-1}\) region. However, the increase and the shift is still smaller than in the case of the treatment dominated by atomic oxygen. The methyl groups are removed in a similar way as during the treatment with ozone. Additionally, absorption around 930 cm\(^{-1}\) and from 3000–3600 cm\(^{-1}\) indicates the presence of new OH, NH and also Si–N–O groups. The XPS measurements of the composition shows that the film contains 3% nitrogen, mainly bonded to silicon. Atomic oxygen causes the most significant changes. Besides the removal of all carbon related absorption features, new Si–O–Si bonds appear and OH absorption is visible in the spectrum. For very large O fluxes to the surface, the deposition rate is more than doubled and denser films with less porosity and OH groups are formed. Among the three species investigated here, the O atom is the most important particle for the generation of SiO\(_2\)-like films.

Acknowledgments

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References

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