Infrared gas phase study on plasma-polymer interactions in high-current diffuse dielectric barrier discharge

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Infrared gas phase study on plasma-polymer interactions in high-current diffuse dielectric barrier discharge

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A roll-to-roll high-current diffuse dielectric barrier discharge at atmospheric pressure was operated in air and Ar/N2/O2 gas mixtures. The exhaust gas from the discharge was studied using a high-resolution Fourier-transform infrared spectrometer in the range from 3000 to 750 cm⁻¹ to unravel the plasma-polymer interactions. The absorption features of HxNyOz, COx, and HCOOH (formic acid) were identified, and the relative densities were deduced by fitting the absorption bands of the detected molecules. Strong interactions between plasma and polymer (Polyethylene-2,6-naphthalate, or PEN) in precursor-free oxygen-containing gas mixtures were observed as evidenced by a high COx production. The presence of HCOOH in the gas effluent, formed through plasma-chemical synthesis of COx, turns out to be a sensitive indicator for etching. By adding tetraethylorthosilicate precursor in the plasma, dramatic changes in the COx production were measured, and two distinct deposition regimes were identified. At high precursor flows, a good agreement with the precursor combustion and the COx production was observed, whereas at low precursor flows an etching-deposition regime transpires, and the COx production is dominated by polymer etching.

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I. INTRODUCTION

Atmospheric-pressure dielectric barrier discharge (DBD) is an excellent candidate for plasma enhanced chemical vapor deposition (PECVD) of functional thin films.1-3 In order to deposit uniform thin films, it is preferable to obtain homogeneous or “glow-like” plasma, which is usually limited to a few noble gases (e.g., helium and argon) under atmospheric pressure.4-6 In our previous research, a high-current “glow-like” discharge was obtained in air-like gas mixture of N2/Ar/O2 under atmospheric pressure.7 The uniformity of the plasma and the high power density make this technology of high applied value in surface treatment as well as in thin film deposition, and excellent SiO2-like barrier layers on polymeric substrates have been achieved.8,9 Distinct regimes of plasma-polymer interactions along the electrodes were identified with AFM and SEM, and it was concluded that during the film growth process a competition between deposition and etching exists.10 It is well known that the deposition, or the polymerization process, is very complex as numerous intermediates such as ions and radicals are generated, which can interact with the polymer surface.11 Quantitative measurements of the reactive species on their ground or excited states were carried out by different spectroscopic methods such as optical emission spectroscopy (OES), laser induced fluorescence (LIF) measurement, mass spectroscopy (MS), and ultraviolet (UV) and infrared (IR) absorption spectroscopy.12-23 Using an ex-situ Fourier-transform infrared (FTIR), Pipa et al. studied the composition of stable molecules from an atmospheric-pressure plasma jet (APPJ) operating in an argon-air mixture.22 The NO production shows a good agreement with other measurements by emission spectroscopy while additional C-related molecules were attributed to plasma contact with the plastic holder of the APPJ. In this study, a high-current “glow-like” discharge was obtained in an open air roll-to-roll system. Infrared gas-phase studies of the plasma exhaust gas were carried out using a high-resolution FTIR spectrometer. The relative densities of the stable species were deduced according to the fitting of the absorption bands of the detected molecules. By varying the gas composition and the substrate, the mechanisms of the molecule production under etching and deposition conditions were discussed. The purpose of the present study is to obtain a better understanding of the gas phase chemical processes with a particular focus on the plasma-polymer interactions.

II. EXPERIMENTAL SET-UP

The schematic pictures of the roll-to-roll plasma reactor with the gas sampling arrangement and the FTIR absorption measurement system are presented in Figs. 1(a) and (b), respectively. In Fig. 1(a), the discharge was ignited between two curved copper electrodes with a radius of 120 mm and a width of 150 mm, both covered by polymeric substrates (Polyethylene-2,6-naphthalate, or PEN) of 100 µm thickness as dielectrics. In this study, two types of the dielectric substrates were investigated. One is bare PEN, and another is PEN coated with a 100 nm thick silica layer. The electrode temperature was sustained at 80°C by means of an oil circulation system. The smallest distance between the two electrodes was 0.5 mm. The gas mixture was injected from the left side of the discharge area in Fig. 1(a), while the substrates were transported at 40 mm-min⁻¹ in the same direction as the gas flow. The flow rate of the gas mixture was controlled at...
about 15 slm (standard liter per minute). However, because of the narrow gap (~100 μm) between the gas injector and the electrodes [see Fig. 1(a)], the gas leakage cannot be avoided. This should be taken into account in the calculations involving the gas flow. In this study, the gas loss is estimated at about 30%. In the deposition, the tetraethylorthosilicate (TEOS) precursor was diluted with 1.0 slm argon together with oxygen as the oxidizer and 15 slm nitrogen as the carrier gas. The DBD was powered by a sinusoidal voltage with a frequency of 185 kHz and amplitude up to 2–3 kV. To reduce the power load to the polymer the injected power was modulated at 625 Hz with a duty cycle of 50%. The input power was kept at 600 W with a power density of about 20 W·cm⁻². A more detailed description of the experimental set-up can be found elsewhere. The effluent gas from the open air reactor was sampled by 10 pipettes into an IR cell (2.5 L volume, 10 cm inner diameter) downstream of the active plasma phase at about 25 mm distance. The flow rate in the extraction system was set to 2.5 slm with about 2.5 s residence time. To increase sensitivity, the IR cell was equipped with a set of spherical mirrors and aligned to a total absorption path length of 700 cm at a reduced pressure of 4300 Pa under room temperature (~25 °C). The IR cell was directly placed into the sample compartment of the FTIR spectrometer [Bruker, IFS 66/s, ~0.15 cm⁻¹ resolution, as shown in Fig. 1(b)]. The etching rate of the polymer substrate was determined by measuring a step profile using a white light interferometric microscope (Veeco, Wyko NT9100) in vertical scanning interferometry (VSI) mode. The surface roughness was measured using an AFM (Park, NX10). Moreover, a particle counter (Lighthouse, SOLAIR 1100 PLUS) with 0.1 μm sensitivity was mounted about 20 cm downstream the plasma reactor to detect the particles after the etching.

III. RESULTS AND DISCUSSION

A. Identification of the absorption spectra

A typical infrared spectrum of the atmospheric-pressure air (15 slm) plasma with bare PEN substrate is presented in Fig. 2. In the range of 3000 to 750 cm⁻¹, only H₂O and CO₂ were detected in the absorption spectrum of the background air. When the plasma was switched on, both N-related species (HNO₂, N₂O, NO₂, NO) and C-related species (HCOOH, CO, CO₂) could be clearly identified. Ozone, which is frequently observed in air-containing DBDs, was not detected under our experimental conditions. The OH radical, detected from OES, was absent here due to its high reactivity, short lifetime, and therefore low density. To acquire quantitative information of the detected molecules from the absorption spectra, the transmission spectra of the molecules except HNO₂ were calculated according to the spectral line parameters given in the HITRAN database using Q-MACSoft-HT software. The HNO₂ spectral line parameters are not available in the HITRAN database. The transmission spectrum of HNO₂ was calculated based on values for the cross section from the Pacific Northwest National Laboratory Northwest IR (PNNL-NWIR) database and by convolving the result with the instrumental broadening. To simplify the data processing, a Gaussian profile with a full width at the half maximum (FWHM) of about 0.15 cm⁻¹ was assumed for the instrumental broadening. The relative density $n$ (number of molecules to the total amount of species, ppm) of the detected molecules were estimated by (manually) comparing the calculated transmission spectra with the measured ones. It is clear that this approach is limited to the small molecules with well-resolved ro-vibrational features. The molecules that were analyzed in this way in conjunction with the spectral range used for the calculation and with their limit of detection for the experimental conditions given earlier are summarized in Table. The detection limit for most molecular species (relative density) is of the order of 10 ppm which corresponds to $10^{14}$ molecule cm⁻³ at atmospheric pressure. These values are based on a signal-to-noise ratio of 1. Typical noise values are 0.5 to 1.5 $×$ 10⁻³ in the transmission spectra. Usually, the error level is a few times higher than the limit of detection. Besides, the overlapping of the spectral lines, e.g., CO, N₂O, and CO₂ in the range from 2300 to 2150 cm⁻¹ also induces errors in the molecule density estimation.

B. Air and air-Ar plasma

For thin film deposition, the plasma is operated in an air-like gas mixture with the addition of Ar as the precursor carrier gas. Because the role of Ar in the gas phase chemistry of the plasma is not known, the relative densities were measured in air (15 slm) and air/Ar (15 slm/1.0 slm) gas mixture with bare PEN substrate. The electrical characteristics are very similar and stable with a single smooth current pulse which indicates a diffuse discharge under both conditions. The corresponding relative densities are shown in Fig. 3. Both N- and C-related species are not significantly changed with the addition of Ar and can be characterized by $\eta$(HNO₂) < $\eta$(N₂O) < $\eta$(NO₂) < $\eta$(NO) and $\eta$(HCOOH) < $\eta$(CO).
&lt;\eta\rangle(CO_2), respectively. This analysis suggests that the addition of Ar is not required to sustain the discharge, and Ar can be used for admixing the precursor without significantly influencing the plasma chemistry.

C. Effect of oxygen concentration

The absorption spectra of Ar/N_2 (1.0 slm/15 slm) and Ar/N_2/O_2 (1.0 slm/15 slm/2.0 slm) gas mixtures with bare PEN substrate are shown in Fig. 4(a). In Ar/N_2 (1.0 slm/15 slm) gas mixture, only CO and CO_2 were detected in the spectrum, and the relative densities of 1500 ppm and 1000 ppm were estimated, respectively. As soon as O_2 (2.0 slm) was injected, &lt;\eta\rangle(CO) and &lt;\eta\rangle(CO_2) increase to 4800 ppm and 10 000 ppm as well as that HCOOH and N-related species (HNO_2, N_2O, NO_2, and NO) appear in the spectrum. The variations of the molecule relative densities with respect to oxygen relative

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Spectral range (cm(^{-1}))</th>
<th>Limit of detection (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO_2</td>
<td>1659, 1274</td>
<td>20</td>
</tr>
<tr>
<td>N_2O</td>
<td>2255-2185</td>
<td>5</td>
</tr>
<tr>
<td>NO_2</td>
<td>1612-1590</td>
<td>5</td>
</tr>
<tr>
<td>NO</td>
<td>1925-1845</td>
<td>20</td>
</tr>
<tr>
<td>HCOOH</td>
<td>1810-1750</td>
<td>10</td>
</tr>
<tr>
<td>CO</td>
<td>2230-2030</td>
<td>10</td>
</tr>
<tr>
<td>CO_2</td>
<td>2270-2260</td>
<td>100</td>
</tr>
</tbody>
</table>

FIG. 2. Identification of stable reaction products in air plasmas with bare PEN substrate: Transmission spectra in the case of (a) plasma off, (b) plasma on, and (c) the calculated spectrum.

FIG. 3. Relative densities of stable molecules in a) air (15 slm) and b) air/Ar (15 slm/1.0 slm) gas mixture with bare PEN substrate.
density in Ar/N₂/O₂ (1.0 slm/15 slm/2.0 slm) gas mixture with bare PEN substrate were estimated, as shown in Fig. 4(b). All N-related products and HCOOH clearly increase with the O₂ content in the gas flow while \( g(\text{CO}) \) and \( g(\text{CO₂}) \) remain relatively stable at about 1 order higher level than the N-related species. Typically, the relative densities for the latter species are all in the order of 100 ppm. With an extrapolation of the increasing trends in Fig. 4(b) to an O₂ flow of about 4.0 slm (i.e., 20% in the mixture as in case of air), the relative densities of \( g(\text{HNO₂}), g(\text{N₂O}), g(\text{NO₂}), \) and \( g(\text{NO}) \) would be \( \sim 200 \text{ ppm}, \sim 300 \text{ ppm}, \sim 500 \text{ ppm}, \) and \( \sim 800 \text{ ppm} \), respectively. These extrapolated results are indeed close to the ones observed experimentally for air/Ar (15 slm/1.0 slm) plasmas in contact with bare PEN substrate (Fig. 3, \( \eta(\text{HNO₂}) \sim 250 \text{ ppm}, \eta(\text{N₂O}) \sim 450 \text{ ppm}, \eta(\text{NO₂}) \sim 650 \text{ ppm}, \) and \( \eta(\text{NO}) \sim 800 \text{ ppm} \)).

**D. N-related reactions**

The relative densities of the main gas phase components in Ar/N₂/O₂ (1.0 slm/15 slm/2.0 slm) plasmas in contact with substrates of bare PEN and PEN covered by 100 nm silica layer are shown in Fig. 5. Both the N- and the C-containing productions vary significantly under the two conditions.

It is well known that the plasma-surface interactions (e.g., etching and deposition) are closely related to the reactive species (e.g., O, O₃, OH, and HO₂) which, in this study, can be reflected by the information of N-related molecules. Therefore, it is important to study the reactions between the HₓNᵧOₗₗ molecules.

The dominant reaction pathways for plasma remediation of HₓNᵧOₗₗ molecules are shown in Fig. 6. Here, the reaction scheme is simplified from Ref. 34 based on the infrared active molecules that are identified in the absorption spectra. These molecules are shown in bold in Fig. 6. In the reaction pathways, NO, which can be regarded as the initial specie, is mainly generated through the reactions between N and oxygen containing species (O₂, OH), as labelled as reaction (1). Then, NO can be remediated through either reduction with N and generating N₂ [reaction (2)], or oxidation with O, O₃, or HO₂ and generating NO₂ [reactions (3), (4), and (5)]. HNO₂, which is generated from the oxidation between NO and OH [reaction (6)], can be further oxidized into NO₂ with enough OH [reaction (7)]. NO₂ can also be reduced with N to produce NO through reaction (8) or N₂O through reaction (9).

In Fig. 5, the relative densities \( \eta(\text{HNO₂}), \eta(\text{N₂O}), \eta(\text{NO₂}), \) and \( \eta(\text{NO}) \) with SiO₂-coated PEN are about 110...
ppm, 280 ppm, 400 ppm, and 1100 ppm, respectively. As soon as the polymer is exposed to the plasma, $\eta(\text{NO})$ decreases to 800 ppm while $\eta(\text{HNO}_2)$, $\eta(\text{N}_2\text{O})$, and $\eta(\text{NO}_2)$ increase to about 275 ppm, 460 ppm, and 680 ppm. This indicates that the H$_2$N$_2$O$_5$ plasma chemistry is influenced by the plasma-polymer interactions. When these interactions occur, the reaction pathways (Fig. 6) are shifted in the direction from NO to NO$_2$ due to enhanced oxidation. The increase in HNO$_2$ with bare PEN further indicates that, OH, which contributes to the generation of HNO$_2$ [reaction (6)], can be produced from reactions with the polymer.

As mentioned before, ozone is absent in the absorption spectrum. It is very likely “poisoned” as, e.g., described in Ref. 1 [reaction (4)] which is supported by the observed levels of NO/NO$_2$ and the absence of N$_2$O$_5$ in the absorption spectrum. Moreover, the ozone generation efficiency decreases drastically under the condition of a high electric field or a high gas temperature.$^{35}$ This is in accordance with earlier characterization of the high power density (10–20 W cm$^{-2}$) plasma when the effective reduced electric field strength ($E/N$) and the gas temperature of the air-like DBD were estimated to be about 150 Td$^{36}$ and 200–300 $^\circ$C,$^{37}$ respectively.

**E. C-related reactions**

**1. CO, CO$_2$ vs HCOOH**

CO and CO$_2$ are well known precursor molecules for the formation of HCOOH in the gas phase in plasma-chemical processes. The HCOOH formation is explained in Ref. 38 through the plasma-chemical synthesis of high initially oxidized mixtures (CO-H$_2$O or CO$_2$-H$_2$),

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{HCOOH}, \quad (3-1)$$

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}. \quad (3-2)$$

Under different conditions, e.g., in oxygen-free or oxygen-containing gas mixtures with bare or silica-coated PEN, we observed a correlation between $\eta(\text{HCOOH})$ and $\eta(\text{CO})$. In Fig. 7, the correlation of the relative densities of CO$_x$ are shown as a function of $\eta(\text{HCOOH})$. Here, $\eta(\text{HCOOH})$ is not controlled but summarized from all the data obtained under different conditions. The production of HCOOH is closely related to those of CO and CO$_2$, and an approximately linear fit of $\eta(\text{CO})$ and $\eta(\text{CO}_2)$ is obtained with $\eta(\text{HCOOH})$. $\eta(\text{CO})$ is about 100 times higher, and $\eta(\text{CO}_2)$ is about 30 times higher than $\eta(\text{HCOOH})$. Moreover, the CO production with bare PEN is much higher than with SiO$_2$ coated PEN, and $\eta(\text{HCOOH})$ does not exceed 50 ppm in the case of SiO$_2$ coated PEN. The mechanism of the carbon-related molecule production will be discussed in Sec. III E 2.

**2. Carbon sources**

To identify the possible carbon sources, the relative densities of CO and CO$_2$ were measured for different plasma conditions: with and without oxygen addition, with bare PEN and SiO$_2$ coated PEN, as presented in Fig. 8.

In the oxygen-free gas mixtures [Ar/N$_2$ (1.0 slm/15 slm)], only a small amount of CO$_x$ is observed both in the case of bare PEN and SiO$_2$-coated PEN. The CO$_2$ production is mainly related to the reactions between oxygen from the ambient air and carbon impurities in the experimental system. These background impurities are inevitable under the current conditions and contribute for about 200–300 ppm to the total production of CO$_x$. The small amount of oxygen results in an oxygen deficient chemistry and consequently a higher production of CO than CO$_2$.

In the oxygen-containing gas mixtures (Ar/N$_2$/O$_2$ (1.0 slm/15 slm/2.0 slm)) with SiO$_2$ coated PEN, the production of CO$_x$ is mainly related to the reactions between the reactive species from the plasma and carbon impurities in the experimental system, e.g., the plastic holders and tubes. Similar carbon impurities were also observed in an APPJ system operating in Ar with 0.1% air.$^{22}$ Moreover, it should be realized that in the present experimental set-up, deposition experiments were operated prior to the current measurements. The organic precursor molecules absorbed on the walls of the experimental system can be desorbed and oxidized in subsequent experiments and therefore contribute to the CO$_x$ production. Since a high relative density of oxygen is present, the carbon impurities in the system can be more

![FIG. 7. Variations of $\eta(\text{CO}_x)$ with $\eta(\text{HCOOH})$ in different gas mixtures and substrates. The open symbols represent the relative densities of carbon products formed after plasma exposure with bare PEN while the solid symbols represent plasma exposure of SiO$_2$ coated PEN. Note, the HCOOH production is not controlled but summarized from the results under the different conditions.](image1)

![FIG. 8. Relative densities of CO and CO$_2$ under different experimental conditions in Ar/N$_2$ (1.0 slm/15 slm) and Ar/N$_2$/O$_2$ (1.0 slm/15 slm/2.0 slm) gas mixtures with bare PEN or SiO$_2$-coated PEN.](image2)
intensively oxidized resulting in a higher $\eta$(CO$_2$) (about 2000 ppm) than $\eta$(CO) (about 1100 ppm).

In the Ar/N$_2$/O$_2$ (1.0 slm/15 slm/2.0 slm) gas mixture with bare PEN, $\eta$(CO) and $\eta$(CO$_2$) increase drastically to about 4500 ppm and 10 000 ppm, respectively. As discussed, the oxidation of the background carbon impurities contributes over 3000 ppm to the total CO$_x$ production. The extra 11 000 ppm of CO$_x$ is therefore due to the interactions between the Ar/N$_2$/O$_2$ plasma and the PEN substrate.

3. Surface etching

It is known that bare PEN can be etched when exposed to an oxygen containing plasma.$^{39}$ To determine the etching rate, the PEN was partly protected by tape and exposed to the air plasma region (with a width of $\sim$15 mm) at a substrate transport speed of 40 mm-min$^{-1}$ equivalent to about 22.5 s exposure time in the plasma. After the plasma treatment, the tape was removed, and the height difference of the step profile was determined using an interferometer in vertical scanning interferometry (VSI) mode, as presented in Fig. 9. In addition, the surface roughness of pristine and etched PEN was measured using AFM, as shown in Fig. 10.

After the plasma treatment, the surface RMS (root mean square) roughness of the PEN increases from $\sim$1.5 nm to $\sim$5 nm (see Fig. 10). The height difference of the step is $\sim$1500 nm which results in an etching rate of $\sim$67 nm-s$^{-1}$. From the amount of the etched PEN, the mass production rate $\Delta m$(PEN) of the polymer can be estimated

$$\Delta m$(PEN) = $\Delta V$(PEN) $\times$ $\rho$(PEN)
= 2 $\times$ $\Delta d$(PEN) $\times$ $l \times v$ $\times$ $\rho$(PEN)
= $4.1 \times 10^{-4}$ g s$^{-1}$, (3-3)

where $\Delta V$(PEN) is the etched volume production of PEN substrate per second, $\rho$(PEN) is the density of PEN (1.36 g cm$^{-3}$), $\Delta d$(PEN) is the thickness of the etched PEN ($\sim$1500 nm), $l$ is the substrate width (150 mm), and $v$ is the transport velocity of the PEN substrate (40 mm min$^{-1}$).

The molecule production rate of carbon $\Delta X$(C) can be estimated as

$$\Delta X$(C) = $\frac{168}{242} \times \Delta m$(PEN) $\times$ $\frac{N_A}{M(C)}$
= $1.4 \times 10^{19}$ molecules s$^{-1}$, (3-4)

where $N_A$ is the Avogadro’s number ($6.02 \times 10^{23}$ mol$^{-1}$), and $M(C)$ is the molar mass of carbon (12 g mol$^{-1}$).

Assuming all the carbon from the etched PEN is fully oxidized and converted to CO$_x$, the relative density $\eta$(CO$_x$) is

$$\eta$(CO$_x$) = $\frac{\Delta X$(CO$_x$)}{\Delta X$(gas flow)$} = \frac{\Delta X$(CO$_x$)$ \times V_m}{\Delta \Phi$(gas flow)$ \times N_A}$ $\sim$ 3300 ppm, (3-5)
where $\Delta X(CO_x)$ is the molecule production rate of CO$_x$ ($1.15 \times 10^{19}$ molecules·s$^{-1}$), $\Delta X$(gas flow) is the molecule flow rate, $\Delta \Phi$(gas flow) is the gas flow rate ($15 \times 0.7$ slm considering a 30% gas leakage), and $V_m$ is the molar volume ($24.5$ L·mol$^{-1}$ at $25^\circ$C).

In Sec. III E 2, we measured $\eta$(CO$_x$) of about $14500$ ppm in Ar/N$_2$/O$_2$ (1.0 slm/15 slm/2.0 slm) plasma with bare PEN substrate. Among the total CO$_x$ production, more than $3000$ ppm is attributed to the oxidization of the background carbon impurities, and the extra $11000$ ppm CO$_x$ is due to the plasma-polymer interactions. The calculated value of CO$_x$ from PEN etching ($\sim 3300$ ppm) is about $3$ times lower than the measured value ($\sim 11000$ ppm). However, the etching should still be the main factor that contributes to the high value of CO$_x$ production. In the above calculation, we assumed that all the carbon from the etched PEN is fully oxidized and converted to CO$_x$. In order to verify this assumption, the exhaust gas was probed by a particle counter during the etching process of bare PEN. A large amount of sub-micron sized particles are detected during exposure of the bare PEN, as presented in Fig. 11. According to Liston et al., etching of the polymer material can take place. Moreover, the etching rate of semi-crystalline polymers such as PEN is preferential, i.e., the amorphous regions have higher etch rate than the crystalline regions [see Fig. 10(b)]. This suggests that in the etching process, small (less than $10$ nm) partially oxidized polymer fragments are produced and agglomerated during transport in the gas flow forming bigger particles ($>100$ nm). The initially airborne particles may attach on the inner surface of the FTIR system (memory effect) and further decompose into CO$_x$ species and thus artificially enhance the FTIR absorption signal. However, not much is known in the polymer interactions with the oxygen-containing plasma. Further studies and more systematic measurements are required to support this hypothesis.

4. Deposition

In addition, the carbon balance was studied under depositions conditions. The relative densities of CO$_x$ were measured with respect to the amount of TEOS added in an Ar/N$_2$/O$_2$ (1.0 slm/15 slm/0.8 slm) gas mixture. The results of the measurements are shown in Fig. 12. The trends of the measured $\eta$(CO$_x$) with TEOS injection can be divided into two regimes. In regime (1), a strong decrease in $\eta$(CO$_x$) with the addition of a small amount of TEOS (less than $100$ ppm) is observed, whereas in regime (2), a clear increase in the $\eta$(CO$_x$) with increasing TEOS flow (more than $100$ ppm) is obtained. This indicates different mechanisms of CO$_x$ production. Moreover, the calculated values of $\eta$(CO$_x$) are approximately the same as the measured ones in regime (2). Hence, the CO$_x$ production in regime (2) can be attributed to the full combustion of the precursor.

As concluded in Ref. 10, the etching and deposition can be competing mechanisms in thin film growth. In regime (2) where the amount of TEOS is relatively high, the etching is weak and the surface of PEN is quickly covered by a SiO$_2$ layer.

The deposition rates are much more complicated. Since the amount of TEOS is relatively low, the surface of PEN is not completely covered by silica layer during the early exposure of the substrate to the plasma region. Oxygen radicals have more time to interact with the polymer surface leading to simultaneous etching and deposition during the film growth process. As discussed in Sec. III E 3, the polymer etching and the generation of a large amount of particles can significantly influence the measurement of $\eta$(CO$_x$) in the FTIR system. Consequently, the CO$_x$ production in regime (1) is dominated by etching, which results in overrated values of $\eta$(CO$_x$), as presented in Fig. 12.

IV. CONCLUSIONS

In this study, the Fourier transform infrared (FTIR) gas-phase analysis of stable molecules in the gas effluent of the atmospheric-pressure plasmas was reported. The absorption features of the plasma species were analyzed. Both N-related species (HNO$_2$, N$_2$O, NO$_2$, NO) and C-related species (HCOOH, CO, CO$_2$) were identified, and the corresponding relative densities were estimated according to the calculations based on the line parameters given in the HITRAN and...
PNL databases. The N-related species were characterized by $\eta(\text{HNO}_2) < \eta(\text{N}_2\text{O}) < \eta(\text{NO}_2) < \eta(\text{NO})$ and reflect the information of the reactive species (e.g., O, O$_3$, OH, and HO$_2$) in the plasma. In the case of bare PEN, the reaction pathways of H$_x$NyOz were shifted in the direction from NO to NO$_2$ due to enhanced oxidation reactions.

The measurement of high rates of CO$_x$ species indicates strong interactions between the oxygen-containing plasma and the polymer (as is produced due to etching of PEN). Formic acid (HCOOH) is identified as a sensitive indicator for plasma-polymer interactions. The sources of CO$_x$ are discussed in relation to the oxidation of the background carbon pollution which contributes about 3000 ppm, whereas the etching of the bare PEN substrate contributes about 11 000 ppm to the CO$_x$ relative density. The estimated values of CO$_x$ cannot be totally explained on the basis of the amount of polymer removed by etching. It is argued that partially oxidized airborne particles are produced during etching that accumulate in the low pressure FTIR cell and subsequently decompose and release CO$_x$ species. By adding precursor (TEOS) in the plasma, two different regimes were identified. At increased precursor flows (above 100 ppm), the production of CO$_x$ is dominated by precursor dissociation and a linear increase of the CO$_x$ species can be directly correlated with the amount of carbon from the precursor combustion. At much lower precursor flows (less than 100 ppm), an etching-deposition regime transpires and etching becomes an increasingly dominant factor in the process.

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