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Plasma–surface interaction at atmospheric pressure: A case study of polystyrene etching and surface modification by Ar/O₂ plasma jet

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In this paper, the authors studied atmospheric pressure plasma–surface interactions using a well-characterized radio-frequency Ar/O₂ plasma jet with polystyrene (PS) polymer films in controlled gas environments as a model system. A number of plasma processing parameters, such as the treatment distance, environmental gas composition, and substrate temperature, were investigated by evaluating both the changes in the thickness and the surface chemical composition of PS after treatment. The authors found that the polymer average etch rate decayed exponentially with the nozzle–surface distance, whereas the surface oxygen composition increased to a maximum and then decreased. Both the exponential decay constant and the oxidation maximum depended on the composition of the gaseous environment which introduced changes in the density of reactive species. The authors previously reported a linear relationship between measured average etch rates and estimated atomic O flux based on measured gas phase atomic O density. In this work, the authors provided additional insights into the kinetics of surface reaction processes. The authors measured the substrate temperature dependence of the PS etch rate and found that the apparent activation energy (E_a) of the PS etching reaction was in the range of 0.10–0.13 eV. Higher values were obtained with a greater nozzle-to-surface distance. This relatively low E_a value suggests that additional energetic plasma species might be involved in the etching reactions, which is also consistent with the different behavior of etching and surface oxidation modification reactions at the polymer surface as the treatment distance is varied. © 2017 American Vacuum Society.

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I. INTRODUCTION

Cold atmospheric plasma (CAP) sources are able to produce chemically reactive species that have been proven effective at modifying material surfaces, sterilizing microorganisms, healing wounds, and even treating cancer. All these applications share an interaction between CAP sources and surfaces, e.g., of polymers, dielectrics, biomolecules, and cells. While an impressive amount of results on CAP source characterization have been achieved, less is known about the mechanisms of plasma–surface interactions (PSIs), especially under atmospheric pressure.

Although one can easily observe CAP induced effects on polymers, cells, and tissues, the difficulty in studying PSI originates from the complex nature of both the gas phase and surface reactions. Unlike thermal plasma, CAP is not in local thermal equilibrium and a wide variety of chemically active conditions can be achieved by changing external parameters such as source geometry, electromagnetic field structure, and gases supplied to the source or in the environment. Compared to low pressure glow discharges, CAP sources have lower cost and relatively simpler designs. This affordability increases the accessibility of CAP to both research and industrial communities, which has in return stimulated numerous new source and power supply configurations. This multidimensional parameter space of CAP not only gives rise to its chemical freedom but also causes difficulties with regard to both characterizing the generated chemical species and establishing standards across CAP’s expanding applications. When a target is present, the rapidly changing fluxes of incident and outgoing species at the material surface interact with each other, which complicates the spatial and temporal profile of plasma species. In addition, PSI frequently involves synergistic effects of multiple reactive species, which adds to the difficulty in interpreting results both computationally and experimentally.

The constant exposure of CAP sources and material surfaces to atmospheric environments further complicates studying PSI. The plasma-environment interaction has a large impact on not only the plasma source behavior but also the species arriving at material surfaces. Controlling the gaseous composition of the CAP source and the PSI vicinity has attracted increasing attention in recent years. For example, by applying a gas curtain around an atmospheric pressure plasma jet (APPJ) operated in humid room air, Reuter et al. were able to reduce the inflow of ambient species...
drastically. Shimizu et al. reported the effect of different humidity levels on the surface microdischarge (SMD) treatment of bacteria using a large environmental chamber (microbiological incubator). In fact, more rigorously controlled environments are desired for the study of PSI because CAP sources are sensitive to even trace impurities.

To understand the mechanisms of PSI, researchers need to establish correlations between reactive species and treated surfaces. This requires a well-characterized CAP source, a controlled gaseous environment, a defined material surface, comprehensive surface characterization techniques, and the understanding of both gas phase and surface reaction kinetics. Early attempts of studying PSI at atmospheric pressure focused on describing the change in the material surface with one or several external parameters of the CAP source, such as power, treatment time, and distance. Two types of changes on surfaces after plasma exposure were distinguished: (1) removal/etching of materials and (2) irreversible modification in the composition/structure of a few molecular layers at or near the surface. For the systematic understanding of etching reactions, the work by Winters to whom this special issue is dedicated, and his colleague Coburn has provided a foundation.

With the progress in CAP characterization, works of correlating gas phase species to either etching or modification have emerged. To achieve the goal of deciphering PSI, joining surface characterization, optical diagnostic techniques, and modeling of an established CAP device is indispensable.

Previously, we have studied the PSI of model polymers and biomolecules with multiple CAP sources such as kilohertz double ring-APPJ, kHz pin-APPJ (Ref. 35), and SMD. We found that surface modification by CAP sources was generic, whereas etching was highly source dependent. More recently, we adopted a well-characterized radio frequency (RF) APPJ whose properties have previously been studied and described, including flow dynamics, gas temperature, electron density and temperature, and density of reactive species such as NO, O, and O3. The reaction pathways of several bio-medically reactive species, including O, O2(a1Δg), H, HO2, OH, N2(A), NOx, and HNOx, generated by this jet have also been obtained by numerical simulations. The available information provides the opportunity for improving our understanding of PSI and interpretation of surface characterization results. By interacting this RF jet with several selected model polymers in highly controlled environments, we correlated polymer etching with O atoms in the gas phase. We found a linear relationship between the incident O flux and the etched C flux of polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(vinyl alcohol) (PVA) in the near plume region of the jet: the etching reaction probability of O atoms to C atoms is in the range of $10^{-4}$ to $10^{-3}$.

In this paper, we further extend our studies of plasma–surface interactions to the far effluent of the Ar/O2 jet. A number of plasma processing parameters, such as the treatment distance, environment gaseous composition, and substrate temperature, are investigated by evaluating the changes in both the thickness and the surface chemical composition of PS after treatment. The role of atomic O on polymer surfaces is discussed. We also evaluate the apparent activation energy of Ar/O2 plasma etching reactions with PS. Finally, we discuss the possibility of polymer etching and surface modification with other plasma species besides atomic O.

II. EXPERIMENT

A. Materials

PS beads were purchased from Sigma-Aldrich (St. Louis, MO) with an average molecular weight of 35 000. Thin films of PS (~180 nm, as measured by ellipsometry) were prepared by spin-coating of 5 wt. % PS in propylene glycol methyl ether acetate (Sigma-Aldrich, ReagentPlus, ≥99.5%) solution at 2000 rpm onto Si substrates (25.4 × 25.4 mm). The C- and H-based pristine PS films contain a negligible amount of oxygen and nitrogen impurities, as measured by X-ray photoelectron spectroscopy system (XPS), which makes it ideal for studying O and N uptake as a result of plasma treatment. These spin-coated PS films have an RMS surface roughness of 0.35 nm as measured by atomic force microscopy (AFM).

B. Plasma processing

The plasma source studied in this work is a time-modulated RF plasma jet. As shown in Fig. 1, the RF jet is composed of three major parts: a 1 mm diameter RF driven tungsten needle, a quartz tube [3 mm outer and 1.5 mm inner diameter (ID)] and a grounded copper ring electrode. The RF signal was generated by a function generator (Tektronix AFG3021B) with a 20 kHz time modulated 14.0 MHz sine wave at a 20% duty cycle (10 µs on, 40 µs off) and then amplified by a power amplifier (ENI A500). The average dissipated power of the plasma jet was measured to be 2 W for the majority of this work using the method described elsewhere. The RF jet feed gas used was Ar plus 1% O2 with a total gas flow of 1.5 standard liters per minute (slm). The average flow velocity of the feed gas can be calculated to be 14.15 m/s. The visible plume length is approximately 3 mm.

![Fig. 1. (Color online) Schematic diagram of the time-modulated RF jet and its interaction with the PS film. The treatment angle $\varphi$ and treatment distance $d$ are adjustable. During material processing, the RF jet scans over the PS surface at a speed of either 1.2 or 2.4 mm/s. The distance between scanning lines is 0.8 mm. The inset shows the RF plasma jet in the vertical ($\varphi = 90^\circ$) configuration.](image-url)
In order to uniformly process large material surfaces, the RF jet was installed on a homemade 2D scanning stage driven by stepper motors. During treatment, the RF jet scans over sample surfaces with a line-by-line processing pattern at a constant speed of 1.2 mm/s unless otherwise noted. The distance between scanning lines is 0.8 mm which is about half of the quartz tube ID. The RF jet scans over the same processing line back and forth and then jumps to the next line. With a total treatment time of 200 s, an area of 9.6 × 9.6 mm can be processed. The RF jet scans 12 times (back and forth) during the entire course of treatment. As shown in Fig. 1, the treatment angle Φ and distance d relative to the material surface are adjustable. In this work, the Φ investigated was 30° (tilted) and 90° (vertical) and distance d from the end of the nozzle to the surface was varied as 4, 8, 12, 16, and 20 mm. We selected 30° for all surface composition analysis using XPS. In order to directly compare etching and surface modification, we performed comparative etching experiments also with a 30° tilt angle. However, we chose theetching data collected at 90° to be correlated with the measured and simulated density of gas phase species, which was also collected at 90°.

The potential heating of the scan-treated target surfaces by the RF jet was evaluated by measuring the thermal expansion of 745 nm SiO\textsubscript{2} during plasma treatment using ellipsometry. We found a temperature increase of less than 20°C for the processing parameters chosen above. We also measured the thickness reduction of PS films due to heating alone, and no observable thickness loss was obtained at 40°C. We observed a thickness reduction of ~2 nm at 80°C, and most of this took place in the first minute. Since the PS samples are always preheated to target temperature before plasma treatment, the effect of heating alone on the etching depth of PS is considered as negligible.

To study the ambient gas composition effect on PSI, the processing of polymer surfaces by RF jet was conducted in both controlled (pure N\textsubscript{2} or N\textsubscript{2}/O\textsubscript{2} mixture) and uncontrolled (humid room air) environments. The controlled environments were achieved using a sealed 50 l chamber that was pre-evacuated to below 50 mTorr and then refilled to atmospheric pressure with high-purity N\textsubscript{2} and/or O\textsubscript{2} gas (Airgas, ~99.998%).

To study the substrate temperature effect on PSIs, a proportional-integral-derivative controlled heating stage was integrated into the controlled environment. PS coated Si wafers were preheated to the desired temperature (30, 45, 60, and 75°C) before scanning treatment. In order to avoid an excessive amount of etching at high temperature, all the temperature dependence experiments were performed with a scanning speed of 2.4 mm/s. The PS thickness loss was evaluated using in situ ellipsometry.

C. Surface characterization

The optical properties of PS films were characterized using both in situ and ex situ ellipsometry with a 1.5 mW HeNe laser (632.8 nm). An optical model was applied to the raw ellipsometric data to extract polymer thickness and refractive index information. To evaluate the etch rate and film densification of PS, in situ ellipsometry was used to acquire the thickness and refractive index in real-time. For scanning processing, the probing laser spot of the ellipsometer was pointed to the center of the treated area. The surface morphology of the PS film was measured using the tapping mode of AFM (Bruker MultiMode AFM).

The surface chemical composition of PS films was characterized using an XPS system (Vacuum Generators ESCALAB MK II) with an Al K\textsubscript{x} X-ray source (1486.3 eV). Both the survey and high-resolution spectra of C 1s, N 1s, and O 1s were obtained at electron take-off angles of 90° (probing depth ≈ 8 nm) and 20° (probing depth ≈ 2 nm). For quantitative analysis, spectra taken at 20° were selected and processed using casaxps software. For the C 1s spectrum, peaks corresponding to C=O (284.7 eV), C–O (286.5 eV), C–O/C (288 eV), O–C=O (289 eV), O–CO–O (290.2 eV), and pi–pi* shake-up (291.6 eV) were used. Due to the overlapping of peaks in the O 1s spectrum, we combined oxygen moieties with binding energy from 532.2 to 533.1 eV into a single peak at 532.7 eV and combined another group of peaks from 533.6 to 535.3 eV into another single peak at 533.9 eV. For the N 1s spectrum, nitroso (401.8 eV) and nitrate (407.5 eV) peaks were fitted. All spectra were calibrated by the C–C/H peak with a binding energy of 285 eV. After Shirley background subtraction, the film composition was calculated by integrating peak areas of C 1s, N 1s, and O 1s with sensitivity factors of 1, 1.77, and 2.85, respectively.

D. Fluid model of the RF jet

A fluid model of the RF jet gas flow combined with reactionless species transport has been created and solved using the commercial Fluent solver (ANSYS Workbench 17.2). The molar ratio of air entrainment into the plasma plume and near the sample surface was investigated. Four treatment geometries, corresponding to the nozzle-sample separations of d = 4, 8, 12, and 16 mm with a tilt angle of Φ = 90°, were simulated. The gas in the fluid model was assumed as an incompressible Newtonian fluid. The turbulent kinetic energy k and turbulent dissipation epsilon (k-ε) model was used to simulate the mean flow characteristics of turbulent flow near the material surface. The governing equations are therefore conservation of mass, momentum, k, and ε. For boundary conditions, the quartz tube of the jet and material surfaces were considered as no slip walls. The inlet gas was selected as Ar + 1% O\textsubscript{2} at 450 K with an average convection velocity of 14.15 m/s (corresponding to 1.5 slm). A constant pressure of 101 325 Pa was chosen for the outlet boundaries. The transport of Ar and O\textsubscript{2} species from the jet inlet into air ambient was simulated through the solution of reactionless convection-diffusion equations for each of the species

\[
\frac{\partial n_i}{\partial t} = -\nabla \cdot \vec{J}_i - \nabla \cdot (\vec{u} \cdot n_i),
\]

where \(\vec{J}_i\) is the diffusion flux and \(\vec{u} \cdot n_i\) is the convection flux of species \(i\).
III. RESULTS

A. Real-time etching profile

In situ ellipsometry was used to evaluate the real time thickness change of PS films during scan-processing with the RF jet. The etching profile of PS with Ar + 1% O2 plasma in the air environment is shown in Fig. 2. The plasma jet was held vertically to the material surface, and four treatment distances from 4 to 16 mm were evaluated. The real time etching curve showed a “staircase” shape, which can be explained by the line-by-line scan processing pattern. Since the size of the ellipsometer probing laser spot (3–4 mm) is larger than the diameter of the RF jet nozzle (1.5 mm) and the scanning steps (0.8 mm), there are cases when only part of the material inside the probing laser spot is etched. These situations are reflected as the artifact of etching steps with a slower etch rate shown in Fig. 2. Real time etching profiles of other plasma chemistries also have a similar “staircase” shape. The real-time etching depth profile in Fig. 2 shows faster etching speed when the plasma jet moved closer to the center of the probing location. In the inset of Fig. 2, we showed the magnified view of the fastest etching step which occurred when the plasma jet was directly over the probing location. The maximum transient etch rate can be calculated from the slope of the etching curves. At a distance of 4 mm, we observed an etch rate of 79.8 nm/min for Ar + 1% O2 plasma in air. Similarly, the maximum etch rate of other treatment distances can also be calculated to be 11.9, 3.62, and 2.14 nm/min for 8, 12, and 16 mm, respectively. However, the accuracy of these instant etch rate calculations is doubtful due to the artifact of the large probing laser spot and decreases at longer treatment distances because of the small transient etch rate. Since we only compare PS treatments with the same scan-processing parameters, the total etching depth which is an indicator of the average etch rate and free of artifact will be discussed in the rest of this paper.

B. Etching depth versus atomic O density

When comparing different treatment distances, we found that the etching depth dropped exponentially with the treatment distance. Figure 3 shows the etching depth of Ar + 1% O2 plasma in both N2 and air environments versus end-of-nozzle to the sample distance. From the absolute etching depth value, we found that Ar/O2 plasma etched more PS in N2 than in air. The etching depth curve in each environment can be empirically fitted by an exponential decay formula with the least-squares method

$$\Delta = A \cdot \exp\left(-\frac{d}{\lambda}\right),$$

where $\Delta$ is the etching depth, $d$ is the treatment distance, and $A$ and $\lambda$ are the fitting coefficients. The empirically fitted $\lambda$, a decay constant, is the distance at which the etching depth is reduced to $1/e$ or 0.368 times of its initial value. For the vertical ($\varphi = 90^\circ$) jet configuration with Ar + 1% O2 plasma in the air environment, we fitted $\lambda_{O2,90^\circ}$ = 2.81 mm with adjusted $R^2 = 0.998$ in contrast to that in the N2 environment where $\lambda_{O2,N2,90^\circ}$ = 4.02 mm and adjusted $R^2 = 0.999$. The smaller $\lambda_{O2,air,90^\circ}$ than $\lambda_{O2,N2,90^\circ}$ indicates that the etching depth decays faster in the air environment than in the N2 environment.

Interestingly, the experimentally measured atomic O density [by two-photon absorption laser induced fluorescence (TALIF) in the air environment] of the same plasma jet with Ar + 2% air plasma also showed a similar decay profile along the plume axis. As shown in Fig. 3, we could fit the measured O density data with the exponential decay formula which yields a decay constant of $\lambda_{O2,90^\circ,measured}$ = 4.06 mm and adjusted $R^2 = 0.971$. The measured atomic O density data are only available up to 6 mm due to the strong collisional quenching at long nozzle-to-sample distances, which makes the TALIF measurements difficult to perform. However, the

![Fig. 2. (Color online) Real-time etching profile of PS treated with Ar +1% O2 plasma in the room air environment. Four treatment distances, 4, 8, 12, and 16 mm, are shown. The gray area shows the in situ film thickness change during plasma treatment. The treatment angle $\varphi$ is 90°. The inset shows the magnified view of the fastest etching step at a treatment distance of 4 mm. The transient etch rate can be estimated as 79.8 nm/min.](image)

![Fig. 3. (Color online) Comparison between the profile of the PS etching depth and that of atomic O density along the treatment distance. Left axis: etching depth of PS treated with Ar + 1% O2 plasma in both N2 and air environments. Right axis: measured atomic O density of Ar + 2% air plasma in the air environment (Ref. 42) and simulated atomic O density of Ar + 1% O2 plasma in the air environment (Ref. 46). Both the etching depth curves and the atomic O density profile fall exponentially with the distance. The treatment angle $\varphi$ was 90°.](image)
simulation result of atomic O density based on GlobalKin for this RF jet with Ar + 1% O₂ feed gas has also been reported before with a distance of up to 12.5 mm.⁴⁶ As plotted in Fig. 3 (open circles), simulated atomic O density shows similar exponential decay behavior with λ_{O₂,ar,simulation} = 2.37 mm which is very close to the decay constant of PS etching depth λ_{O₂,ar,90°} = 2.81 mm. Both the measured and simulated atomic O density profiles correlate well with the etching depth profile, which suggests that atomic O might be the main etchant for Ar + 1% O₂ plasma.

C. Surface morphology and chemistry

The RF jet treatment also modified the morphology and chemical composition of the polymer surface in addition to inducing etching. AFM was used to study the surface morphology before and after RF jet treatment. As shown in Fig. 4, the pristine PS film has a RMS roughness of 0.35 nm. After Ar/O₂ plasma treatment in the N₂ environment with a distance of 8 mm, the thickness of the PS film reduced by 29.5 nm and the RMS roughness increased to 3.24 nm. The features of Ar/O₂ treated PS film are also more distinct.

The surface chemical composition of PS films was characterized by XPS. To illustrate the change on PS surface moieties, high resolution C 1s, N 1s, and O 1s spectra of pristine and Ar + 1% O₂ plasma treated PS films are shown in Fig. 5. Plasma treatment was performed at 8 and 16 mm in the N₂ environment with a tilted jet configuration (φ = 30°). Since the PS structure has long hydrocarbon chains wherein alternating carbon centers are attached to phenyl groups, the C 1s spectrum of the pristine sample shows 91.1% C–C/H bond (285 eV) and 5.4% of π-π* shake-up (291.6 eV, phenyl ring) with a negligible amount of O and N.

After treatment, the etched PS surface showed oxidation but no NO uptake for both distances. From the C 1s spectrum [Fig. 5(a)], we found that plasma treatment induced destruction of the C–C/H bond and the phenyl ring as well as the formation of C–O, O–C–O=C=O, O–C=O, and O–CO–O groups. The relatively large amount of carbonate ester (O–CO–O) group is a distinctive feature of the RF jet etched polymer films compared to other CAP sources we have studied, including surface microdischarge and double-kilo-hertz APPJ. Correspondingly, in the O 1s spectrum [Fig. 5(b)], a peak at 533.9 eV is observed and can be assigned to this carbonate ester group. As to the N 1s spectrum [Fig. 5(c)], a peak at 402.7 eV is observed and can be assigned to the amine group.

D. Ambient gas composition effect on etching and modification

To understand the effect of the environment gas composition on PSI, we evaluated the etching efficiency of Ar/O₂ plasma in controlled environments consisting of various O₂/N₂ mixtures. The studied O₂ concentration ranges from 0% to 100% (N₂ concentration varies accordingly), and all treatments were performed at 4 mm with a tilted configuration (φ = 30°). The average plasma power was 3.8 W, and the scanning processing speed was 2.4 mm/s. As shown in Fig. 6, the polymer etching depth and the absolute value of its slope decrease with the environmental O₂ concentration. These changes in the etching depth with the environment gas composition are largely due to the gas entrainment, especially the O₂ component, which alters the flux of reactive species impinging the target surfaces. The relative amount of O₂ entrainment in the plume increases with the environmental O₂ composition, which causes the drop in the etching depth as shown in Fig. 6. More discussions about the effect of O₂ entrainment can be found in Sec. IV C.

To further understand the effect of ambient gas entrainment on PSI, we studied the treatment distance response of both etching and surface modification of PS films processed in room air and N₂ environments. Because the high resolution XPS data showed that all treated films exhibited the same type of functional group that differed only in the relative amount, we presented the elemental compositions extracted from these high resolution XPS data for the ease of discussion. As shown in Fig. 7, one generic observation for both environments is that the etching depth dropped exponentially with the treatment distance, but the corresponding surface oxygen composition reached a maximum at intermediate distances and then decreased. This is mainly because the density and dominant type of reactive oxygen species (ROS) change as a function of distance from the nozzle. Although the etching depth can be easily correlated with atomic O, the increase in the surface oxygen composition is hard to interpret. Among the dominant ROS generated by this RF jet, i.e., O, O₂(a^1Δg), and O₃, only O₂ density increases with the nozzle-to-sample distance. However,
previous reports\textsuperscript{50,51} have shown that O$_3$ alone has a weak and slow oxidative effect on polymers and UV light is frequently required for effective surface treatment. This suggests that the observed surface oxidation could be due to other ROS or the synergistic effect of a few types of ROS including O$_3$. The observed increase in the surface oxygen composition from 4 to 12 mm is most likely due to the competition between surface etching and modification processes rather than the ROS density profile of one plasma species. More details about the surface kinetic process are discussed in Sec. IV D.

The observed difference in the etching depth between Figs. 3 and 7 results from not only the treatment angle effect but also the experimental uncertainty due to the changes in the experimental setup. Since changing treatment angle requires the adjustment of the RF jet on the scanning stage which slightly varies the treatment distance, the resultant etching depth of polymer films might differ by 10–20 nm at a treatment distance of 4 mm considering the exponential decay behavior of the etching depth along the nozzle-to-sample distance. Although we are unable to conclude in detail how the treatment angle affects polymer etching behavior, the difference seen between $\phi = 30^\circ$ and $\phi = 90^\circ$ is much smaller than that in changing feed gas chemistry reported previously.$^{43}$

We also found that using the air environment rather than N$_2$ had a relatively small influence on both the etching depth and the surface oxidation. This can be seen from the absolute etching depth and the empirically fitted decay constant as $\lambda_{O_2,air,30^\circ} = 3.63$ mm compared to $\lambda_{O_2,N_2,30^\circ} = 4.15$ mm with only a difference of 0.52 mm. Although the surface oxygen composition of films treated in the two gas environments falls in the same range of 20%–30%, the maximum surface oxygen composition appears at different treatment distances of 8 mm and 12–16 mm for N$_2$ and air environments, respectively. In the N$_2$ environment, all surface oxygen originates from the feed gas of the plasma jet. In the air environment, the O$_2$ entrainment from ambient can change the density profiles of certain reactive species, which may lead to the shift in the surface oxidation maximum shown in Fig. 7.

In order to gain more insight into the gas entrainment effect, fluid dynamic (FD) simulation was performed to calculate the molar fraction of air mixed into the RF jet plume. Figure 8 shows the simulated air molar fraction at the sample surface for four treatment distances (4–16 mm). It can be seen that the amount of air mixture is only dramatically different within a 4 mm radius circle on the material surface. At the surface beyond this 4 mm circle, the air mole fraction is comparable for all treatment

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**Fig. 5.** (Color online) High resolution XPS (a) C 1s, (b) N 1s, and (c) O 1s spectra of PS treated by the RF jet with Ar + 1% O$_2$ plasma at 8 and 16 mm in the N$_2$ environment. Pristine PS is also shown for comparison. The treatment angle was 30°.

**Fig. 6.** Environment gaseous composition effect on the PS etching depth treated with Ar + 1% O$_2$ plasma. All treatments were performed at a distance of 4 mm with a tilted configuration ($\phi = 30^\circ$) and a plasma power of 3.8 W. The scan-processing speed was 2.4 mm/s.

**Fig. 7.** (Color online) Comparison between air and N$_2$ environments on the etching depth and surface oxygen composition of the PS film treated with Ar + 1% O$_2$ plasma. The treatment angle was 30°.
distances and always higher than 60%. Because we used 0.8 mm steps between scan-processing lines, the gray area (0–0.4 mm off the axis) in Fig. 8 shows the scale of the line-scan processing steps. At the plume axis, only 2.9% molar fraction of air was observed at a treatment distance of 4 mm. However, for longer distances, the amount of air mixture increases exponentially to 70.5% at 16 mm as shown in the inset of Fig. 8. These FD simulation results agree well with the air partial pressure measured by molecular beam mass spectrometry (MBMS) with the same plasma jet. Although a large difference in the amount of gas entrainment was observed between near and far treatment distances, the difference in the etching depth between two environments in Figs. 3 and 7 (black solid and black dotted lines) is small and does not change significantly with the treatment distance. This indicates that the polymer etch rate and the density of etchant plasma species may not respond linearly to the amount of environmental gas entrainment in the plasma core. Similar behavior can also be seen in Fig. 6 as the etching depth at 4 mm becomes constant when the ambient gas composition is more than 50% of O2. The initial small amount (less than 2%) of gas entrainment has a much greater influence on the plasma gas chemistry and its subsequent effect on the polymer than the further increase of it.

E. Substrate temperature effect

The substrate temperature effect on the PS etching depth was evaluated with a vertical jet configuration in the N2 environment. Three distances, i.e., 4, 12, and 20 mm, were evaluated. We found that the etching depth of PS treated with Ar + 1% O2 plasma increased with temperature (or decreased with 1/Tsub, as shown in Fig. 9).

IV. DISCUSSION

A. Apparent activation energy of the etching reaction

The increase in the etch rate at higher temperatures indicates that polymer etching by the RF jet is an activated process. For the ease of discussion, we can use the following formula to represent the conglomeration of all interfacial reactions:

\[
\text{Etchant}(g) + \text{Surface}(s) \rightarrow \text{Product}(g) + \text{Surface}^*(s),
\]

where Surface* is the etched surface and \( k_{ER} \) is the apparent rate constant of all etching reactions. If we use the Arrhenius equation to describe the temperature dependence of rate constant \( k_{ER} \), then we have

\[
k_{ER} = A_{ER} \cdot \exp\left(\frac{-E_a}{k_bT}\right),
\]

where \( A_{ER} \) is the pre-exponential factor, \( k_b \) is the Boltzmann constant, and T is the substrate temperature. The apparent activation energy \( E_a \) is an empirically fitted parameter that represents the effective activation energy of various reactions taking place during the etching process. The \( E_a \) value for a given polymer/gas system can be a function of processing parameters such as plasma power, gas flow rate, and treatment distance. Since the total etching depth can be directly correlated with the rate constant \( k_{ER} \), we obtained apparent activation energy \( E_a \) by plotting the logarithm of the etching depth against \(-1/k_bT\). As long as the affinity of etchant species on the material surface and \( E_a \) do not change with temperature, a linear fitting can be achieved.

As shown in Fig. 9, the apparent activation energy of Ar + 1% O2 plasma slightly increases with the treatment distance and falls in the range of 0.10–0.13 eV which is lower than the \( \sim0.5 \) eV value reported consistently with pure O2 low pressure plasma with various polymer structures or etching configurations. Despite the difference in plasma properties between CAPs and low pressure plasma, this lower \( E_a \) value suggests that the energy barrier of the etching process may have been reduced by some additional energetic...
plasma species. There are multiple possibilities for such species in our situation, including positive ions which were observed previously by MBMS for the same plasma jet. These energetic species can (1) transfer energy and momentum to the surface and cause particle ejection and (2) change the coverage of chemically reactive elements on the surface and/or the rate of refreshment. However, at this time, we do not have enough information to state conclusively that energetic species are directly involved, let alone identifying what these energetic species are and the detailed reaction processes. Nevertheless, other explanations are possible, and we will report further investigation on the relationship between apparent activation energy and treatment conditions of CAP sources.

It is worth noting that polymer etching and temperature effects are highly source dependent. We have investigated another CAP source known as SMD using similar approaches, and with the substrate at room temperature, we did not observe etching with N2/O2 mixtures as working gas. Key differences between these sources are the higher O density in the effluent, the use of Ar which can give rise to energetic species, and the convective transport of gas phase species in the case of the RF jet.

B. Etching reaction probability of atomic O

Plasma etching of polymers usually starts from free-radical site creation through bombardment by UV photons, electrons, ions and chemical reaction with gas phase atoms or excited species. Among these creation channels, H-abstraction by atomic O from the polymer chain has been discussed by different research groups as the most important channel for both low pressure plasma and atmospheric pressure plasma. Key differences between these sources are the higher O density in the effluent, the use of Ar which can give rise to energetic species, and the convective transport of gas phase species in the case of the RF jet.

In order to evaluate the relationship between PS etching and atomic O species in the gas phase, we estimated the average O flux bombarding the PS surface from the atomic O density data in Fig. 3 by using Eq. (6) from the kinetic theory of ideal gases

$$\Gamma = \frac{1}{4} n \bar{v} = \frac{1}{4} n \sqrt{\frac{8RT}{\pi M}},$$

where \(\Gamma\) is the average gaseous flux, \(n\) is the gas density, \(\bar{v}\) is the average speed, \(R\) is the gas constant, \(T\) is the gas temperature, and \(M\) is the atomic weight of O. For the atomic O density measured by Van Gaens et al., the density and gas temperature values used at 4, 6, and 8 mm are \(8 \times 10^{15} \text{ cm}^{-3}\) and 420 K, \(6 \times 10^{15} \text{ cm}^{-3}\) and 390 K, and \(2 \times 10^{15} \text{ cm}^{-3}\) and 375 K, respectively. For the atomic O density simulated by Wende et al., the density and gas temperature values used at 4, 8, and 12 mm are \(4.2 \times 10^{15} \text{ cm}^{-3}\) and 420 K, \(1.8 \times 10^{15} \text{ cm}^{-3}\) and 375 K, and \(0.45 \times 10^{15} \text{ cm}^{-3}\) and 320 K, respectively. The average etched C flux from the PS surface was calculated from the measured etching depth by Ar + 1% O2 plasma in the air environment. Since PS only contains C and H and the ratio C:H is 1, the total amount of etched C atoms (\(N_c\)) over the whole scan processing period can be estimated as

$$N_c = \frac{\Delta \cdot A_{\text{treated}} \cdot \rho}{A_C + A_H} \cdot N_A,$$

where \(\Delta\) is the etching depth in Fig. 3, \(A_{\text{treated}}\) is the scan processed area (0.922 cm²), \(\rho\) is the density of PS (1.04 g/cm³), \(A_C = 12\) and \(A_H = 1\) are the atomic mass of carbon and hydrogen atoms, and \(N_A\) is Avogadro’s number. Although the PS surface was scan treated, most of the etching occurred under the direct exposure of the RF jet plume. At any moment, the transient processed area can be approximately viewed as the cross-sectional area of the jet nozzle (\(\pi/4\cdot\text{ID}^2\)). Therefore, the average etched C flux can be estimated as

$$\Gamma_c = \frac{N_c}{\pi/4 \cdot \text{ID}^2 \cdot t},$$

where ID is the inner diameter of the RF jet quartz tube (1.5 mm) and t is the total processing time (200 s).

As shown in Fig. 10, by plotting the incident O flux and removed C flux together, we found a linear correlation between the two at treatment distances up to 12 mm. The etching reaction probability of O atoms can be estimated from the fitted slope in Fig. 10 and is found to be in the range of \(2 \times 10^{-4} - 4 \times 10^{-4}\). This order of magnitude is comparable to the p values of H abstraction probability by O atoms shown in Eq. (5) and published work. It is also consistent with the values that we have formerly reported by measuring the etching of three polymers, i.e., PS, PMMA, and PVA, with higher plasma dissipated power (~3.5 W) and faster scan-processing speed (2.4 mm/s).

C. Exponential decay of the etching depth along the treatment distance

The exponential decay of the etching depth indicates that the flux of etchant species bombarding the material surface...
might also drop exponentially with the treatment distance. The plasma etching process involves (1) the chemical reactions taking place at the gas–solid interface and (2) the transport of reactants to the reaction front. It is usually the latter that limits the overall reaction rate. Although the interfacial reactions are inherently complex, the average time needed for etching reaction steps is at the level of picoseconds, e.g., a few picoseconds for H-abstraction and tens of picoseconds for C–C/O bond cleavage. Therefore, the density of etchant species near the gas–solid interface can be considered to be proportional to the etching depth. From Eq. (2), the density of etchant species [etchant] can be expressed as

\[ [\text{etchant}] = A' \cdot \exp \left( -\frac{d}{\lambda} \right), \]  

where \( A' \) is the pre-exponential factor and \( \lambda \) is the same decay constant as in Eq. (2).

The exponential decrease of etchant species in Ar/O\(_2\) plasma, presumably atomic O, along the nozzle-to-sample distance is mainly a result of local generation and consumption of O atoms although these reactions might also be influenced by forced convections. The lifetime of atomic O can be estimated from the temporally resolved O density measurement with the same RF jet (reported by Zhang et al.) with Ar + 2% O\(_2\) in the air environment used in this work, which leads to a lifetime of 0.2–0.3 ms. The apparent lifetime \( t_a \) of atomic O can be defined by the exponential decay constant through

\[ t_a = \frac{\lambda}{v_{\text{flow}}}, \]

where \( \lambda \) is the decay constant in Eq. (9) and \( v_{\text{flow}} = 14.15 \text{ m/s} \) is the average feed gas velocity. For etching by Ar + 1% O\(_2\) plasma in N\(_2\) and air environments (Fig. 3), we could calculate the apparent lifetime of \( t_a, N_2, 90^\circ = 0.284 \text{ ms} \) and \( t_a, \text{air}, 90^\circ = 0.199 \text{ ms} \) from the decay constant of \( \lambda_{\text{O}_2, N_2, 90^\circ} = 4.02 \text{ mm} \) and \( \lambda_{\text{O}_2, \text{air}, 90^\circ} = 2.81 \text{ mm} \), respectively. These \( t_a \) values agree well with the atomic O lifetime of 0.2–0.3 ms estimated from the published results by Zhang et al.

The difference in the exponential decay constant between N\(_2\) and air can be attributed to the O\(_2\) and H\(_2\)O entrainment from ambient air. According to the simulation results by Van Gaens and Bogaerts in the far effluent region, the atomic O is mainly consumed through O\(_3\) generation reaction

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \\
k = 6.40 \times 10^{-35} \exp(663.0/T_{\text{gas}}) \text{ cm}^6 \text{ s}^{-1},
\]

whereas in the plume region, water impurities can have a large impact on the atomic O kinetics, which might lead to over 80% of the total loss of atomic O. It is worth mentioning that atomic O can also be generated locally in the afterglow region up to 15 mm by the collisions between O\(_2\) and O\(_3\) with the rate coefficient

\[
\text{O}_2(a^3 \Delta_g) + \text{O}_3 \rightarrow 2\text{O}_2 + \text{O} \\
k = 5.2 \times 10^{-11} \exp(-2840/T_{\text{gas}}) \text{ cm}^3 \text{ s}^{-1}.
\]

Simulation results suggest that this is a slow O release process and can be responsible for almost all O generation in the far effluent region.

**D. PSI: Possibility of other plasma species besides atomic O**

The data presented in this work indicate that the etching and modification of polymers by the RF plasma jet involve surface interactions with multiple plasma species. In order to illustrate this, we correlated the PS etching depth and the surface oxygen composition with the incident atomic O flux, as shown in Fig. 11. The measured etching depth and surface oxygen composition are abstracted from Fig. 7, and the corresponding atomic O flux is calculated from the fitted atomic O density from simulation (blue dotted line) in Fig. 3 using

\[ [\text{atomic O}] = C \cdot \exp \left( -\frac{d}{\lambda} \right), \]  

FIG. 11. Correlation of etching and surface modification of PS (in terms of etching depth and surface oxygen composition, respectively) with estimated atomic O flux impinging the PS surface. The PS films were treated with Ar + 1% O\(_2\) plasma in the air environment.
the method described in Sec. IV B. Figure 11 shows that the etching depth of PS has a relatively simple relationship with the flux of atomic O, which we have correlated in Sec. IV B. However, the surface oxygen composition of PS shows a rather complex behavior with the impinging atomic O flux, which can be varied by adjusting the nozzle-to-surface distance. This suggests that either the O related surface reactions are complex or there are other important quantities besides atomic O. The additional plasma species, if present, might exhibit a different behavior with a nozzle-to-surface distance from atomic O, which is consistent with the fact that the apparent activation energy varies as the nozzle-to-surface distance is increased. Besides, the decrease in the surface oxygen composition with the increase in atomic O flux shown in Fig. 11 suggests that etching and modification might not be entirely independent: the etching process might impede the accumulation of surface modification by removing oxidized sites. We are currently working on a detailed PSI model that considers these factors, and we will report it in the near future with further experimental evidence.

V. SUMMARY AND CONCLUSIONS

In this paper, we studied atmospheric pressure plasma-polymer surface interactions using a well-characterized RF Ar/O$_2$ plasma jet and PS as a model system. The surface response of PS to a number of plasma processing parameters, namely, treatment distance, environmental gas composition, and substrate temperature, was characterized by evaluating both the thickness and surface chemical composition change after treatment. Kinetics of surface reactions were discussed and correlated with the plasma gas phase.

We showed that the Ar/O$_2$ RF plasma jet can induce fast etching and mild oxidation of the PS surface. We found that the etching efficiency of Ar/O$_2$ plasma dropped exponentially with the nozzle–surface distance. The correlation of the etching depth profile of PS with the density profile of atomic O measured/simulated in the gas phase indicates that atomic O can be the dominant etchant species. The etching reaction probability of atomic O is estimated to be in the range of 2 × 10$^{-4}$–4 × 10$^{-4}$. Different from the etching depth profile, we showed that the surface oxygen composition of PS reached a maximum and then fell down with the treatment distance. The difference between etching and surface oxygen composition profiles along the treatment distance implies that surface etching and modification can be controlled by different interfacial processes involving multiple plasma species.

The apparent activation energy ($E_a$) of the etching reaction was estimated by measuring etch rate versus substrate temperature. We measured the apparent activation energy of Ar/O$_2$ plasma etching reaction with PS, and it is in the range of 0.10–0.13 eV and increases slightly with the treatment distance. This relatively low $E_a$ value suggests that additional energetic plasma species might be involved in the PSI processes. This is also consistent with the different behavior of the etching and modification reactions at the polymer surface as the nozzle-to-surface distance is varied.

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