

RF Jet Treatment of Polymers as a Case Study of Plasma-Surface Interactions at Atmospheric Pressure

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Cold atmospheric plasma (CAP) sources produce chemically reactive species that effectively modify material surfaces. While impressive source characterization results have been published, less is known about the interaction mechanisms of these sources with surfaces. To correlate measured gas phase species and changes on material surfaces, we applied a well-characterized radio frequency (RF) plasma jet [1] to surface modification of polystyrene (PS) in a highly-controlled environment. The outcome is a better understanding of plasma-surface interaction mechanisms at atmospheric pressure [2].

Treatment distance, angle, gas feed and environment gas compositions were investigated.

Both polymer thickness and surface chemical composition were evaluated after treatment. We compared the effect of different plasma species on polymer surfaces. The etching reaction probability of atomic O and OH radicals (Fig. 1a) were evaluated by correlating gas phase species density (measured with TALIF for O and LIF for OH) and etching of PS, and found to be $\sim 10^{-4}$ and $\sim 10^{-2}$ for O and OH, respectively. For both Ar/O₂ and Ar/H₂O plasmas (Fig. 1b) the species densities and etch rates of PS decayed exponentially with treatment distance, whereas surface oxidation increased to a maximum and then decreased. Polymer etching and surface modification by Ar/O₂ or Ar/H₂O plasma jets behave differently with treatment distance and the gaseous environment, indicative of the roles of additional species at the polymer surface that control surface oxidation/etching. A surface reaction model based on the competition between O, OH and another species can reproduce the experimentally observed opposing trends. This work presents the first detailed correlation gas phase species measurements and resulting etching and surface modification, and applies to polymers, biomolecules, cells and other model surfaces.

References

- [1] W. V. Gaens, P. J. Bruggeman, A. Bogaerts, *New Journal of Physics* **16**, 063054 (2014).
- [2] P. Luan, A. J. Knoll, H. Wang, V. S. S. K. Kondeti, P. J. Bruggeman, and G. S. Oehrlein, *J. Phys. D. Appl. Phys.* **50**, 03LT02 (2017);

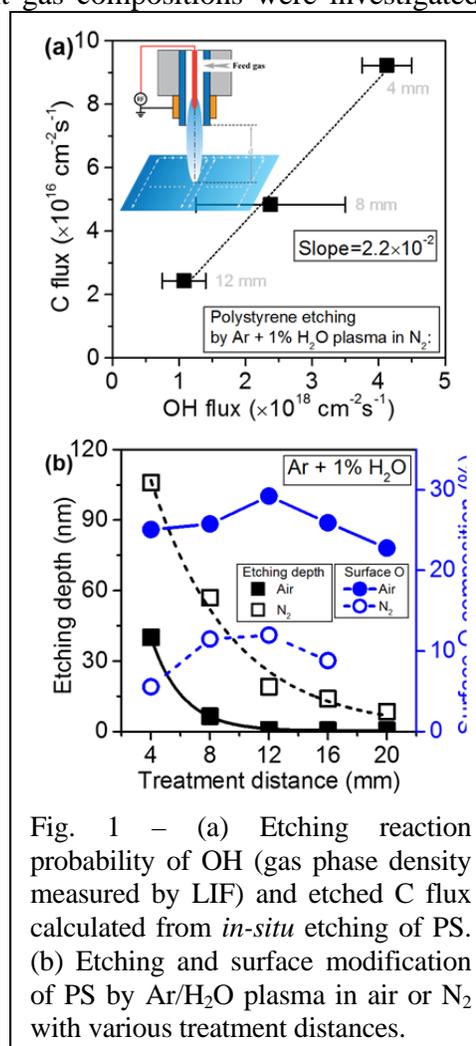


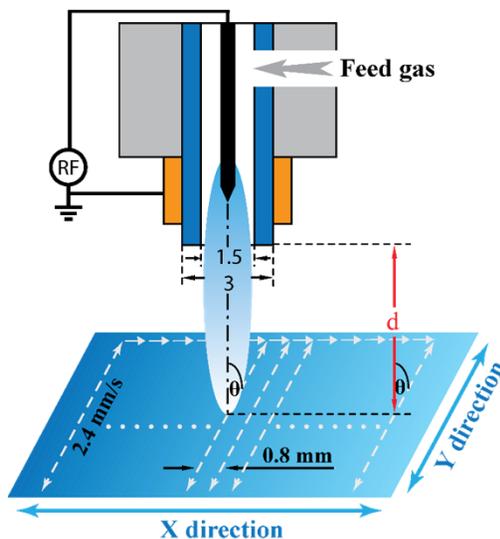
Fig. 1 – (a) Etching reaction probability of OH (gas phase density measured by LIF) and etched C flux calculated from *in-situ* etching of PS. (b) Etching and surface modification of PS by Ar/H₂O plasma in air or N₂ with various treatment distances.

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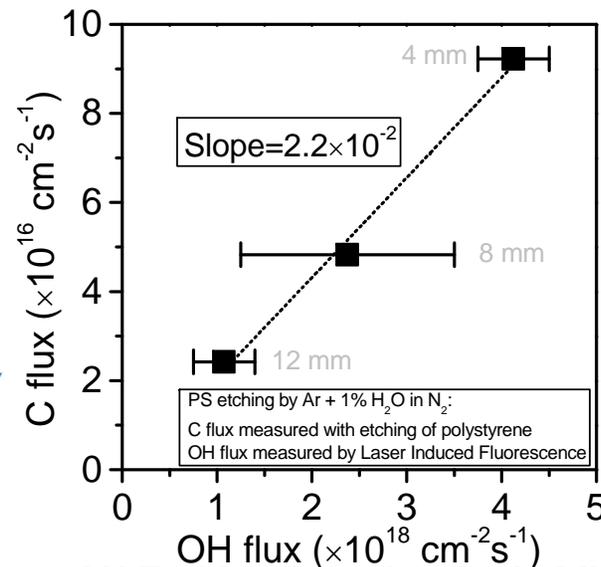
Highlight

PLASMA-SURFACE INTERACTION (PSI) AT ATMOSPHERIC PRESSURE

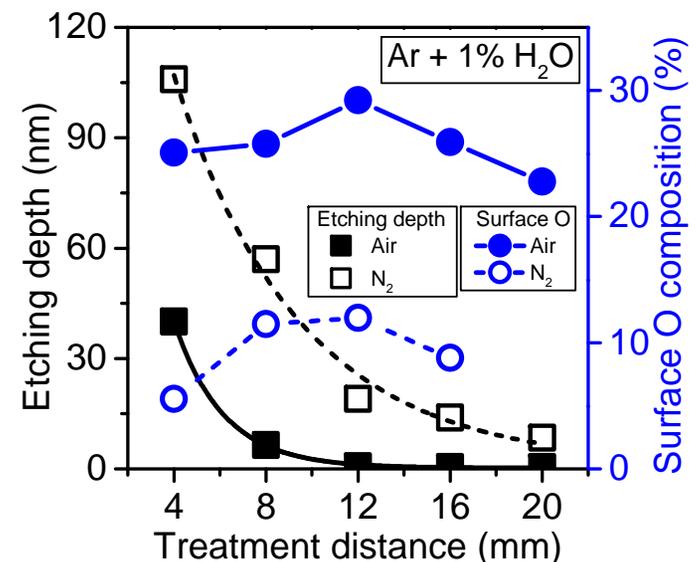
- We use polymer treatment with a cold atmospheric pressure RF plasma jet as model system for elucidating complex plasma-surface interactions (PSI)
- The etching reaction probability of atomic O and OH radicals with polystyrene was evaluated by correlating gas phase densities (TALIF for O and LIF for OH) and etching, and found to be $\sim 10^{-4}$ and $\sim 10^{-2}$ for O and OH, respectively.
- Polymer etching and surface modification by Ar/O₂ or Ar/H₂O plasma jets behave differently with treatment distance and gaseous environment, indicative of the roles of additional species at the polymer surface.



• Treatment by RF Plasma Jet



• OH Etching Reaction Probability



• Etching vs. Surface Modification

Ionization Instability Induced by Nonlocal Electron Kinetics in Atmospheric Pressure Plasmas

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Atmospheric pressure plasmas (APPs) have wide-ranging energy and biomedical uses, and reproducibility for these applications requires discharge stability. Using fully kinetic particle-in-cell (PIC) simulations, we discovered spatially unstable behavior in helium discharges with trace H₂O vapor [1]. We confirmed this for 1–4 mm gap rf (27 MHz) and DC-driven discharges [2], and, more recently, at low frequencies (50 kHz). We also found an even stronger spatial instability in argon with trace H₂O. (See Fig. 1.) Noble gas/trace gas collisions are complex, involving attachment, rotational and vibrational excitations and dissociation. PIC simulations with modified collision processes allowed us to decouple the “physics” from the complicated chemistry. We verified that the instability is induced by high electron recombination rates with heavy water cluster ions (e.g., H₁₃O₆⁺). We found that the ionization rate coefficient K_{iz} varies inversely with the reduced electric field E/N_g in the PIC simulations, leading to instability. These trends are indications of nonlocal electron kinetics, a surprising result in these highly collisional plasmas.

To demonstrate this nonlocal behavior, we recently determined the electron heating kinetics from the simulations. As seen in Fig. 1 for an Ar/1%H₂O mixture, electron Joule heating $J \cdot E$ does not equal the collisional loss P_{coll} within the striations, and we observe a significant electron heat flux dH/dx , indicating significant electron non-locality. We are currently developing a “first-principles” kinetic theory based on the two-term expansion of the Boltzmann equation for these phenomena. In a fully non-local theory of the electron kinetics, we find that K_{iz} can vary inversely with E/N_g , as seen in the PIC simulations.

We have seen instability stabilization in the PIC simulations. Short wavelengths can be stabilized by ion diffusion, and long wavelengths can be stabilized by a finite discharge length, or by a transition to local electron kinetics, in which K_{iz} increases with increasing E/N_g .

We are currently investigating two crucial questions for APP applications:

- (1) What are the necessary and sufficient conditions for instability stabilization?
- (2) Do instabilities appear in other noble gas/trace gas systems such as Ar/O₂ or Ar/dry air, which also contain high mass ion clusters such as O₄⁺?

References

- [1] E. Kawamura, M.A. Lieberman and A.J. Lichtenberg, *Plasma Sources Sci. Technol.* **25**, 054009 (2016)
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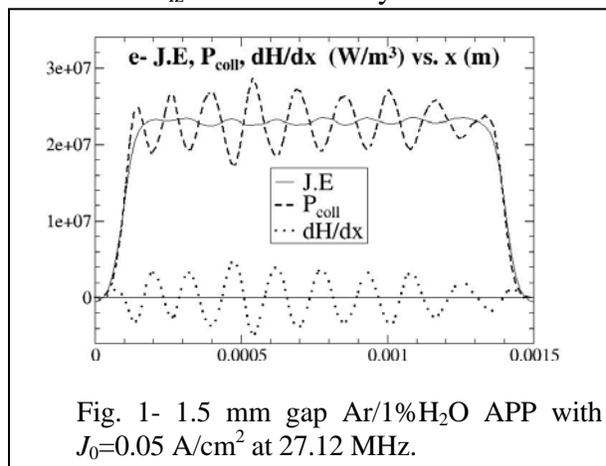
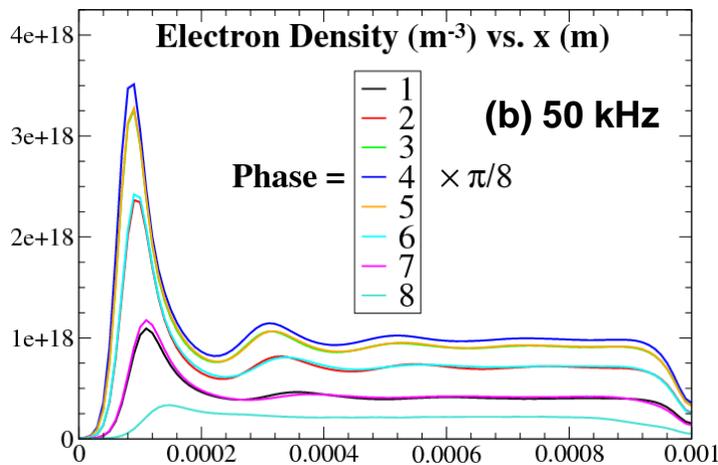
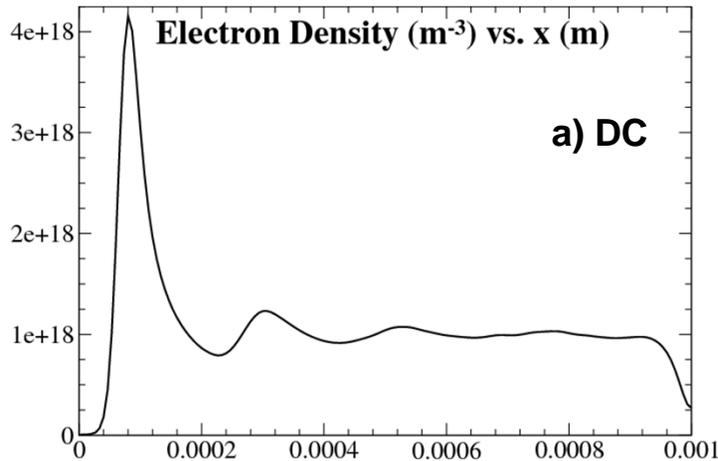


Fig. 1- 1.5 mm gap Ar/1%H₂O APP with $J_0=0.05$ A/cm² at 27.12 MHz.

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Highlight

INSTABILITIES IN ARGON AND LOW FREQUENCY HELIUM APPs WITH TRACE H₂O VAPOR



- 1 mm gap He/2%H₂O APP with $J_0=0.23$ A/cm²
(a) DC and (b) phases in a 50 kHz half-cycle.

- APP energy and biomedical applications require discharge stability.
- Kinetic PIC simulations show ionization instabilities (striations) in rf, dc, and low-frequency driven narrow gap (1- 4 mm) He/2%H₂O APPs.
- A theory with parameters from the PIC indicates that instabilities are due to high recombination rates of water cluster ions (e.g., H₁₃O₆⁺), induced by non-local electron kinetics.
- Comparing DC and 50 kHz driven He/2%H₂O APPs, instabilities grow quasistatically as the electron density increases ($s_{\text{instab}} > 50$ kHz).
- Ar/H₂O APPs are more unstable due to reduced ion diffusion stabilization.