

Model Polymer Etching Mechanisms and Surface Modification by a Time-Modulated RF Plasma Jet

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Cold atmospheric pressure plasma jets (APPJs) are able to generate chemically reactive species desired for material processing and biomedical applications. A great amount of attention has been devoted to characterizing these APPJ sources and expanding their applications. Less is known on the interaction mechanisms between cold atmospheric pressure plasma and material surfaces. Since both plasma sources and material surfaces are constantly exposed to the surrounding ambient, the gaseous environment is coupled with the plasma and material surface and influences plasma-surface interactions. The lack of quantified reactive species measurements for these plasma sources also impedes the interpretation of material surface response with plasma treatment.

In this work, surface interaction of a well-characterized time modulated radio frequency (RF) plasma jet [1] with model polymers, namely polystyrene, poly(methyl methacrylate) (PMMA) and poly(vinyl alcohol) (PVA), is investigated using a controlled gaseous environment. The RF plasma jet has been previously studied in detail including its biochemically reactive species densities [2] such as NO, O and O₃ which provides a unique opportunity to improve the understanding of plasma surface interaction. We find that the RF jet can induce fast organic material etching, whereas X-ray photoelectron spectroscopy after vacuum transfer only detects minor surface chemical modifications of the polymers, including slight oxidation. This is in contrast to surface interaction mechanisms with other atmospheric pressure plasma sources (e.g. surface micro-discharges). The measured etch rates and surface chemistry reflect plasma treatment conditions (e.g. feed gas, environment, treatment distance). In particular, we find that etching depth mirrors the measured decay of O atoms in the gas phase as the nozzle-surface distance increases. The etching reaction probability of O atoms with C atoms ranges from 10⁻⁴ to 10⁻³ and is consistent with low pressure plasma research. The elucidation of the role of oxygen atoms in polymer etching was possible, since the source operating conditions were chosen so that other surface interaction mechanisms (O₃, VUV, direct filament interaction) were negligible.

References

- [1] S. Hofmann, et al., *Plasma Sources Science & Technology* **20**, 065010 (2009).
 [2] S. Q. Zhang, et al., *Journal of Physics D-Applied Physics* **46**, 205202 (2013).

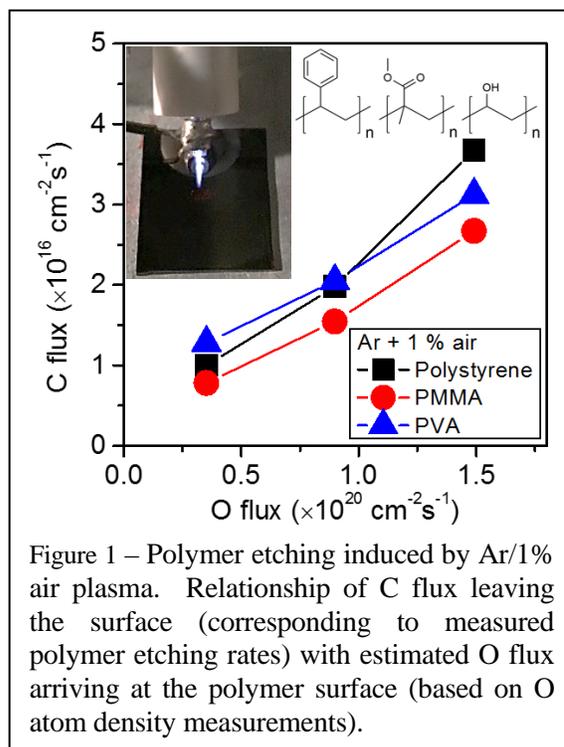
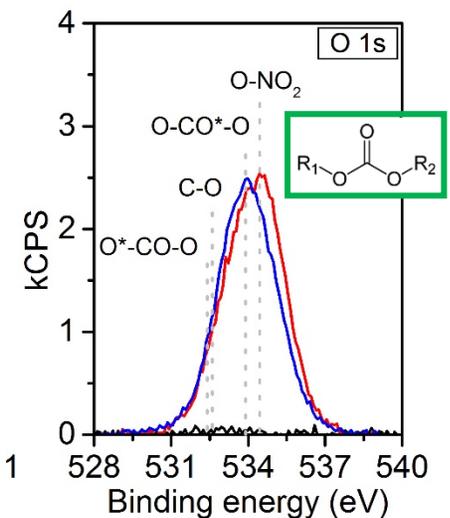
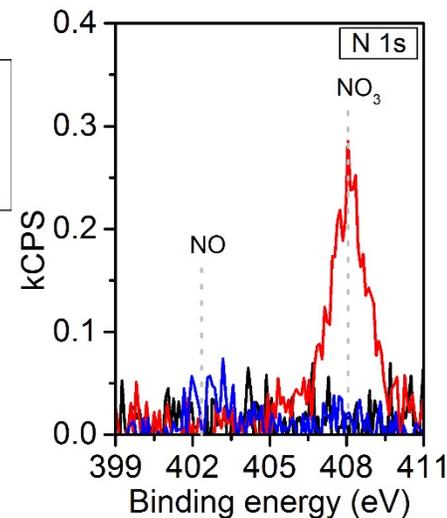
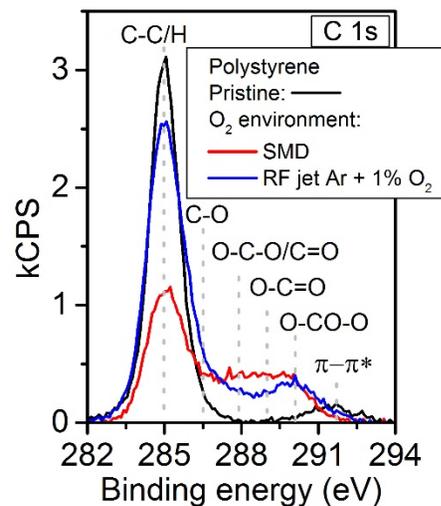
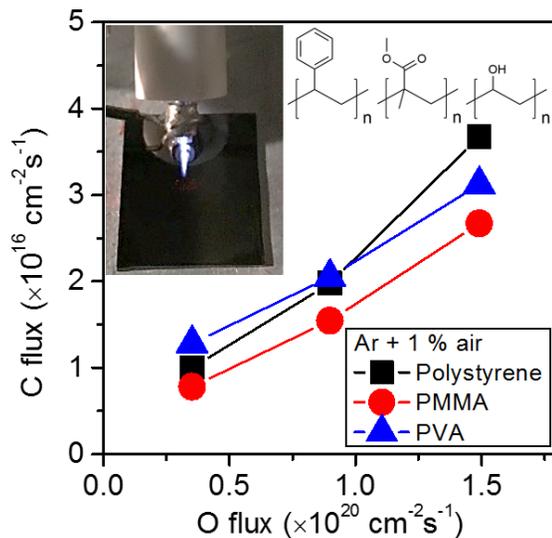


Figure 1 – Polymer etching induced by Ar/1% air plasma. Relationship of C flux leaving the surface (corresponding to measured polymer etching rates) with estimated O flux arriving at the polymer surface (based on O atom density measurements).

MODEL POLYMER ETCHING MECHANISMS AND SURFACE MODIFICATION BY A TIME-MODULATED RF PLASMA JET

- Surface interactions of a RF plasma jet with model polymers are investigated.
- The RF jet induces fast polymer etching but mild chemical modification with carbonate ester (O-CO-O) rich surfaces in contrast to other atmospheric pressure plasma sources, such as the surface micro-discharge (SMD).
- Atomic O and OH radicals initiate polymer etching for Ar/O₂ and Ar/H₂O plasmas. The etching reaction probability of O atom with C atom is found to be between 10⁻⁴ and 10⁻³.



• Estimated etching probability

• Surface modification comparison: RF jet vs. SMD

Kinetic Global Modeling framework: V&V and Metastable Rare Gas Laser

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Similar to diode-pumped alkali metal lasers (DPALs), electronically excited states of rare gases (e.g. Ar and Kr) have been shown to operate as a chemically inert three-level gain media for an optically pumped laser system.[1] DPALs operate on the vapor pressure of a metal whereas rare gas lasers (RGLs) rely on an electric discharge in a rare gas to efficiently maintain a population of metastable states which act as the lower laser level. Alkali metal vapor with the commonly used methane buffer gas potentially produce corrosion and alkali hydrates which could dampen laser performance. RGLs with a helium buffer do not have these limitations. Though the original RGL experiments were performed with pulsed optical pumping within an excimer laser cavity, more recent experiments have shown that CW operation can be achieved using a microplasma array.[2] The smaller microdischarge cavities enable a high electric field strength while reducing the risk of localized breakdown and kinetics bottlenecks when operating near atmospheric pressures.

The Kinetic Global Modeling framework (KGMf) has been developed to investigate this class of plasma chemistry, and was applied to the investigation of optically pumped RGLs. The plasma and gas phase chemistry modules within the KGMf were first verified against similar models in the literature, and then validated against experiments once a complete reaction set could be defined. An intracavity laser intensity module was implemented and validated against the experimental work of Rawlins et al.[2] Though these systems have been studied computationally, it is typically in the context of assuming steady-state operation and fixed rates.

Using the KGMf as an investigative tool, we propose that a modified electron energy distribution (EED) can be used to tune rare gas laser efficiencies, as might occur during pulsed operation. This analysis was made possible by accounting for EED variability on rate coefficients during pulsing. For example, Ar excited state densities during optically pumping of an Ar:He RGL system equilibrating from initial conditions are shown in Fig. 1. With parameter scanning methods, optimized system parameters and EED characteristics can be determined. Baselines for traditional modes of RGL operation are being compared to different variations of microwave and optically pulsed power. These studies will be enhanced by further development of a Boltzmann equation solver integrated within the KGMf will enable a consistent determination of EEDs.

References

- [1] J. Han and M.C. Heaven, *Opt. Lett.*, **28**, 2336 (2012).
- [2] W.T. Rawlins et al. *Opt. Express*, **23**, 4804, (2015).

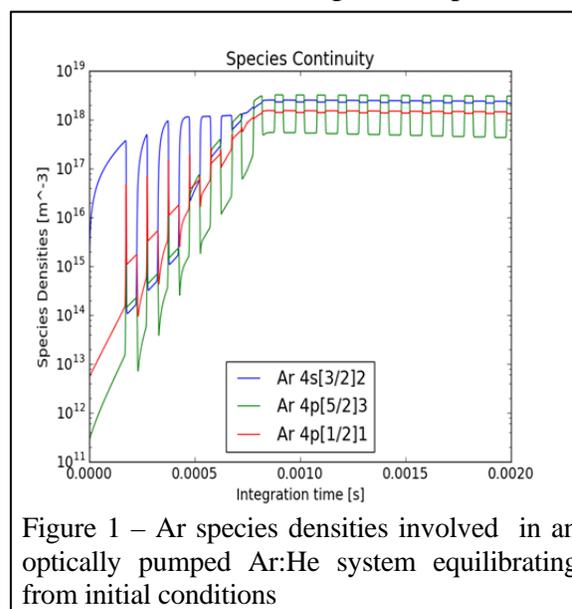


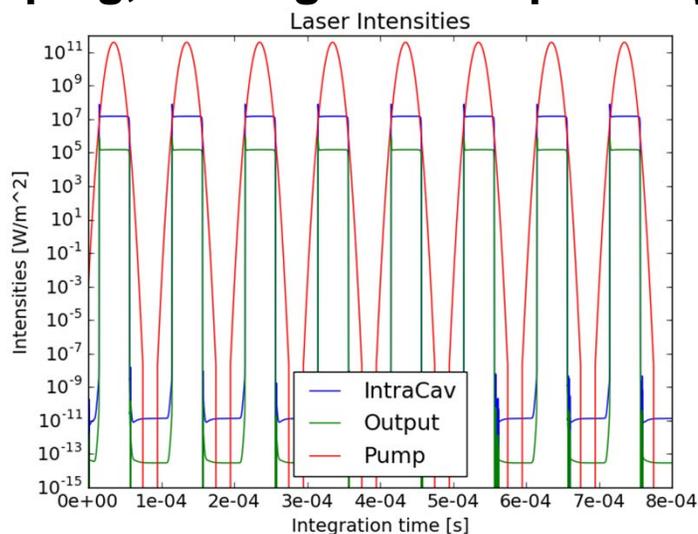
Figure 1 – Ar species densities involved in an optically pumped Ar:He system equilibrating from initial conditions

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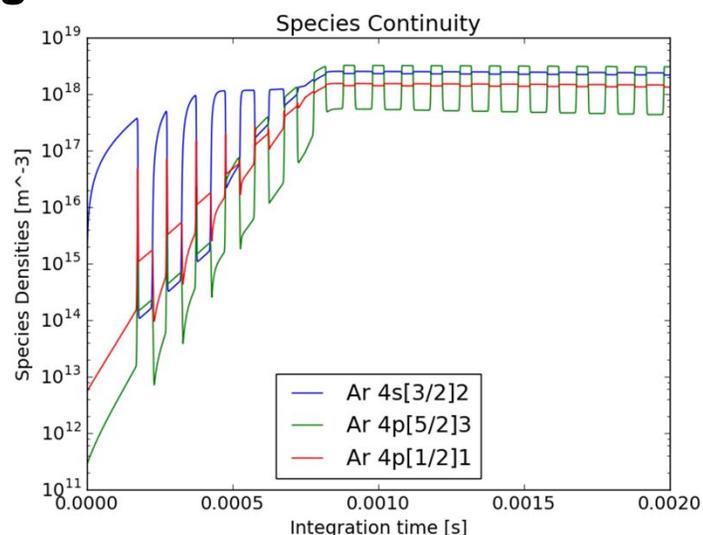
Highlight

KINETIC GLOBAL MODELING FRAMEWORK (KGMf): V&V and METASTABLE RARE GAS LASER

- Optically pumped rare gas lasers (RGLs) are being investigated with the KGMf.
- The KGMf has been verified for low to atmospheric pressure plasma chemistry and validated with complete confirmed mechanisms and reaction sets.
- An intracavity laser intensity was added to the KGMf and validated for continuous wave (cw) RGL pumping in Ar and Ar:He using microplasma arrays.
- RGL performance on EED, pulsed microwave (MW) excitation and optical pumping, and higher level pathways is being characterized



- Laser intensities for pulsed operation with pure Ar



- Ar densities with cw MW, and pulsed optical pumping.