Atmospheric Plasma Treatment of Polymers by Long-Lived Reactive Neutrals

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Cold temperature N₂/O₂ atmospheric pressure plasma (APP) devices produce chemically active species that are the basis of many applications involving treatment of materials [1]. Less is known about the reactive species that are instrumental to this treatment; in particular the role of long-lived reactive neutrals, and how they interact with materials.

To obtain an understanding of APP/surface treatment mechanisms for a prototypical case, we quantitatively correlated the measured responses of plasma-treated vinyl model polymer materials with the surface arrival rate of measured gas phase species. These measurements were made for a kHz surface micro-discharge (SMD) reactor fed with various N₂/O₂ gas chemistries [2]. Long-lived reactive O₃, N₂O₅, N₂O and HNO₃ were found to be the dominant species and were related to polymer treatments. A strong structural dependence of polymer modification by these species was found and is shown in Fig. 1a. For methyl, alcohol, ether based polymers, materials were removed by prolonged treatment at a slow rate. In contrast, for styrene-based polymers, the film thickness increased to a maximum and then decreased. Attenuated Total Reflectance (ATR)-FTIR and x-ray photoelectron spectroscopy (XPS) were used to understand the changes of SMD-treated polystyrene (PS) films (Fig. 1b). The destruction of aromatic rings (labeled A through H in Fig. 1b) and the formation of ether, ester (shaded area I through IV in Fig. 1b) and surface organic nitrate groups take place. Correlation of PS thickness/chemical composition changes with fluxes of plasma generated reactive species indicate that O₃ causes destruction of PS aromatic rings and produces carbonyls. This increases film thickness since oxidized moieties are less tightly packed than styrene rings. In Fig. 1c, we show the surface O elemental composition of SMD-treated PS films versus the dose of O₃ delivered to the PS films. The exponential increase followed by saturation of surface oxidation indicates is due to the depletion of polymeric reactants.

References

Figure 1 – (a) The thickness change of polymers resulting from exposure to SMD effluents. (b) ATR-FTIR spectra of polystyrene treated vs. SMD treatment time. IR peaks A through H come from aromatic rings. (c) The correlation of PS surface O elemental composition and the dose of O₃ received.
The effect of long-lived reactive neutrals from atmospheric pressure N$_2$/O$_2$ plasmas on polymers was studied by correlating gas and surface properties.

Fourier-transform infrared spectroscopy (FTIR) shows O$_3$, N$_2$O$_5$, N$_2$O, HNO$_3$ as major reactive species from N$_2$/O$_2$ surface micro-discharge reactor (SMD).

Ellipsometry, attenuated total reflectance-FTIR and X-ray photoelectron spectroscopy (XPS) show that plasma effluents produce aromatic ring cleavage and oxidation. Ozone fluxes correlated to the material composition.
Symmetry Breaking in High Frequency Symmetric Capacitive Discharges

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In spontaneous symmetry breaking, a symmetric physical system excited symmetrically gives rise to an asymmetric equilibrium state. Although the equations of motion obey symmetries, the stable equilibrium solutions do not. When the system goes to one of those solutions, the symmetry is broken. We discovered an example of symmetry breaking in the dynamics of high frequency, large area, capacitively coupled plasma (CCP) discharges [1]. Two radially propagating surface wave modes, symmetric and antisymmetric, can exist in these discharges. In the former, the upper and lower axial sheath electric fields are aligned, while in the latter, they are opposed. For a symmetric (equal electrode areas) CCP driven symmetrically, we expected to observe only the symmetric mode, leading to a symmetric equilibrium. However, when the drive frequency is above the antisymmetric mode spatial resonance, we find that both wave modes can be excited, leading to a non-symmetric equilibrium.

We used a fast 2D axisymmetric fluid-analytical code to examine a 3 cm gap, 20 cm diameter, symmetric CCP operated in the frequency range of 55 to 100 MHz at low pressure (7.5 mTorr) and low plasma density (~3 x 10^{15} m^{-3}). The frequency range encompasses the first antisymmetric radial resonance frequency \( f_a \), but is well below the first symmetric resonance frequency. For frequencies below \( f_a \), the symmetric CCP is in a stable symmetric equilibrium. A typical result at 60 MHz for the sheath widths at the bottom (solid) and top (dashed) electrodes is shown in Fig. 1a. At higher frequencies, a non-symmetric equilibrium appears (e.g., Fig. 1b at 80 MHz).

We developed a nonlinear lumped circuit model of the symmetric CCP to understand these results. The sheath nonlinearity induces symmetry breaking excitation of the antisymmetric mode in this symmetric system. The circuit model results agree well with the fluid simulations.

References
SYMMETRY BREAKING IN HIGH FREQUENCY CAPACITIVELY COUPLED PLASMAS (CCPs)

- In spontaneous symmetry breaking, a symmetric system excited symmetrically gives rise to an asymmetric equilibrium state. We discovered symmetry breaking in symmetric (equal area electrodes), high-frequency driven CCP’s.
- Two radially propagating wave modes, symmetric and antisymmetric, can exist in symmetric CCP’s. In our 2D fluid simulations, we only expected to observe a symmetric mode and equilibrium state (e.g., 60 MHz, Fig. 1a).
- At frequencies above the first antisymmetric resonance, we found both modes can be excited, leading to a non-symmetric equilibrium (e.g., 80 MHz, Fig. 1b).
- We developed a nonlinear lumped circuit discharge model that agrees well with the fluid simulations. The nonlinearity induces the symmetry breaking.

Fig 1 - Contour plots showing poloidal current $I = 2\pi r H_\phi$ at (a) 60 MHz and (b) 80 MHz