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## Energetics of reactions in a dielectric barrier discharge with argon carrier gas: Halocarbons

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The novel method we developed for understanding energy exchanges between argon (Ar) carrier gas and precursor molecules in a large-area ( $216 \text{ cm}^2$ ) dielectric barrier discharge (DBD) reactor has resulted in a series of articles, each relating to a different family of organic compounds. This communication focuses on two new groups, perfluorocarbons, ( $C_xF_y$ ), and perchlorocarbons, ( $C_xCl_y$ ), and compares results with earlier ones for hydrocarbons, ( $C_xH_y$ )[1] and hydrofluoromethanes, ( $CH_xF_y$ )[2].

The precursors (in parts per thousand concentrations) were mixed with Ar in a 20 kHz, 8 kV (peak-to-peak) DBD. For each separate compound, the energy absorbed per molecule ( $E_m$ , in eV), was determined from measurements of the time resolved discharge current,  $I_d$ , and the gap voltage,  $V_{gap}$ . Plotting  $E_m$  as a function of precursor flow rate,  $F_d$ , and also  $1/F_d$ , allows for the identification of the maxima,  $(E_m)_{max}$ , identifying the boundary between the so-called "monomer-lean" and "monomer-rich" operating regimes. It has been highly instructive to plot  $(E_m)_{max}$  values as a function of atomization enthalpy ( $H_f$ ) or alternatively molar mass (MM): in the case of saturated hydrocarbons, for example, this results in straight-line plots with rising MM or  $H_f$ , while the trend was not as clear cut for halocarbons.

The process generally led to thin "plasma polymer" (PP) deposits (e.g. on Si wafer substrates). Their characteristics, like their C/F or C/Cl composition ratios from XPS measurements, strongly correlated with  $E_m$  and  $F_d$ , as did PP deposition rates and water contact angles.

[1] B. Nisol et al., Plasma Process Polym, 2016;14:e201600191.

[2] S. Watson et al., Plasma Process Polym, 2020;17:e201900125.

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