Canadian Association of Physicists
Association canadienne des physiciens et physiciennes

Contribution ID: **251** Type: **Oral not-in-competition (Graduate Student) / Orale non-compétitive (Étudiant(e) du 2e ou 3e cycle)**

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

Wednesday 9 June 2021 16:10 (15 minutes)

The novel method we developed for understanding energy exchanges between argon (Ar) carrier gas and precursor molecules in a large-area (216 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 $(E_m)_{max}$x 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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Session Classification: W3-5 Plasma processes for material synthesis I (DPP) / Procédés de plasmas pour la synthèse de matériaux I (DPP)

Track Classification: Plasma Physics / Physique des plasmas (DPP)